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The Stress Relaxation of Fibrous Materials*

I. Instrumentation and Preliminary Results

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Abstract

An apparatus has been built to study the relaxation behavior of wool, silk, and nylon as a function of reagent temperature, concentration, and hydrogen ion concentration. In distilled water all three materials show the same behavior over most of the time range studied—that is, a gradual relaxation of perhaps one-third of the initial stress, attributable in all likelihood to the destruction of hydrogen bonds. When the water is replaced by sodium bisulfite solution at pH 6.5, the rate of stress relaxation of wool keratin increases markedly. This change is attributed to the scission of the disulfide cross-links in this material by the sulfite ion, in view of the finding that silk and nylon, which are free of cystine, are not affected by sodium bisulfite.

Further experiments on wool have been made to show the effects of solutions of hydrochloric acid, urea, thioglycolic acid, and cysteine. The addition of 0.1*M* HCl to an extended fiber relaxing in water produces a sharp drop in the stress; but the stress returns to its previous value when the acid is replaced with water. When 0.1*M* hydrochloric acid is replaced by sodium bisulfite solution at pH 1.2, the rate of stress relaxation is much slower than that observed with sodium bisulfite at pH 6.5. The addition of 10*M* urea to a fiber relaxing in water produces a relatively slow decay of stress. When the 10*M* urea solution is replaced by a solution of 0.1*M* sodium bisulfite in 10*M* urea, the rate of stress relaxation is more rapid than that produced by sodium bisulfite alone. Cysteine and thioglycolic acid solutions at pH 6.5 produce an approximately exponential decay of stress when added to wool fibers previously relaxed in water.

Introduction

The experimental technique used in the work presented here consists of extending the material under consideration by a predetermined amount, and observing the subsequent decay of stress (or force) as a function of time. In many instances the resulting stress-time curves are susceptible to mathematical analysis in terms of physical or chemical rate processes, and yield information about the structure and mechanical behavior of the polymer. In those cases where a scission of cross-links in the system is brought about by chemical action, the assumption is generally made that the relaxation of stress is controlled by this chemical process, any physical process

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such as molecular rearrangement being assumed to occur much more rapidly. Then a convenient means is available for measuring the rates of chemical reaction in systems that otherwise might be difficult to study.

Stress-relaxation techniques have been employed in the investigation of polysulfide rubbers [17, 32], and the results have been interpreted in terms of certain metathetic interchanges between the various polysulfide cross-links and sulfhydryl groups within the structure. Another application of the stress-relaxation technique is the investigation of the scission and the cross-linking effects of molecular oxygen on rubber systems containing a hydrocarbon main chain [33–35]. In this case the assumption is made that the cross-linking reactions occur in such a manner that they do not influence the decay of stress. This condition requires that the cross-links enter the structure in positions which are stress-free with respect to the extended sample; then the decay of stress is controlled only by the rupture of network chains. Thus, interestingly enough, the stress-relaxation technique should be able to separate scission and cross-linking reactions which occur simultaneously. The investigation of the polyisobutylene system [1] is an example where the mathematical analysis of the experimental data yielded by this technique is more complicated than in those cases cited above.

In view of the investigations just mentioned and those of Speakman [26] on keratin fibers, it seemed that an attempt should be made to investigate systematically the stress-relaxation behavior of wool keratin under a wide variety of experimental conditions. Keratin is a naturally occurring fibrous protein which is predominantly amorphous in character, as shown by x-ray diffraction experiments. The "backbone" of the structure is composed of amino acids joined together by peptide linkages [9, 11]. The resulting polypeptides are held together by several types of interchain bonds. They are: (*1*) hydrogen bonds, formed mainly between the amide and carbonyl groups of the polypeptide chain; (*2*) secondary bonds that arise from van der Waals' forces; (*3*) the covalent disulfide bonds of cystine residues [2]; and probably (*4*) the "salt bridges" [28] between charged free amino and carboxylic groups. Under the assumption that stress relaxation of wool keratin is controlled by the scission of cross-links [12, 26], an evaluation of the kinetics can be made if one can separate the contributions of these cross-links to the relaxation behavior. Furthermore, there must be considered the role of the relatively bulky side-groups of amino acid residues in the relaxation processes. For the moment, the relationship between stress-relaxation behavior and the morphological structure is ignored.

There are two avenues through which the separation of the effects of the various cross-links may be reached. The first involves the use of reagents which are specific for a given type of bond, whereas the second requires the use of materials which differ in the nature of their cross-link systems. Fortunately, practical experiments in both directions can be carried out.

In the first case, reagents are available which are sufficiently specific for the bonds in wool keratin to enable the data to be interpreted in terms of chemical kinetics. Various reducing agents are available (*e.g.*, sodium bisulfite, thioglycolic acid, and cysteine) which react with the cystine disulfide bond and probably do not affect appreciably the hydrogen bonds and "salt bridges" during the time of reaction.* Hydrogen-bond breaking reagents, such as urea or guanidine hydrochloride, may be used to investigate the effects of removing hydrogen bonds from the stress-supporting network. Finally, the action of acids, bases, and neutral salts can be studied to determine the nature of the "salt effect" and its relation to "salt bridges" of the molecule.

In the second case, materials are available which have less complicated types of cross-links within the molecule, but have a similar general chemical structure of backbone. For example, silk fibroin contains no cystine or cysteine and few ionizable amino and carboxylic groups. With this material, then, an investigation can be undertaken to determine the effects of the reducing agents upon the hydrogen-bonded polypeptide chain. As another example, nylon may be used to determine whether the amino acid side-chains present in silk and wool, but absent in nylon itself, have any effect upon the relaxation processes. Nylon is a polyamide and is probably cross-linked solely by hydrogen bonds, although it does contain a free amino and carboxylic group at each end of the chain. If the assumption is valid that the stress-relaxation behavior of these materials at constant strain is controlled by the scission of hydrogen bonds in the amorphous regions of these

* A possible exception to this statement is the "salt effect" reported by Katz and Tobolsky [12] and Speakman and Whewell [30], but this action is relatively slow and should not affect the kinetics at short times.

polymers, rather than by some physical flow process, then silk, nylon, and wool should show many similarities in behavior. Unfortunately, there is available in this laboratory no material that contains a large number of free amino and carboxylic groups without appreciable quantities of cystine. A possibility in this direction is to make use of keratins modified so that a great majority of the stress-supporting cystine linkages are converted to lanthionine bonds, or otherwise made unreactive toward reducing agents.

Accordingly, it is seen that by the proper combination of reagents and materials it may be possible to cast some light upon the chemistry and molecular structure of keratin. It must be kept in mind, however, that a complicated system is involved, and any discussion of an experimental procedure is an idealistic one. On the one hand, the reagents are not so specific as could be desired. An example is the "salt effect" produced by neutral salts. This effect, which appears with such solutes as sodium and potassium chloride, will probably be found in some degree when reducing reagents are used. On the other hand, it is likely that the differences which do exist between materials selected in view of their similarity in a specific aspect will have some effect on the relaxation behavior. For example, nylon and silk have a different type of crystallite structure from wool, and this difference may play an important role in the stress-relaxation behavior of these materials. Nonetheless, it is believed that the possible fruitfulness of this technique outweighs its shortcomings and that this mode of attack will provide systematic and worth-while information that can be correlated with the structure and chemistry of fibrous materials.

Instrumentation

Stress-relaxation experiments on various plastic materials at constant strain have been carried out by a number of workers using devices of varying complexity. The main features of any instrument for this technique will be a force-measuring unit and a means for extending the sample a definite amount and maintaining this strain during the course of the experiment. Simple examples of such apparatus are given by Tobolsky, Prettyman, and Dillon [35], Katz and Tobolsky [12], and Speakman and Shah [29]. More elaborate devices have been described: Stein and Schaevitz [31] have devised an autographic stress relaxometer utilizing the linear variable differential transformer (*LVDT*) or "microformer"; Lundgren [14] has built a multi-unit apparatus based on resistance strain gages in a bridge circuit; Beste [5] has described an instrument using Statham Wire Strain Gages*; Reese and Eyring [20] have used an instrument which is a modification of the Sookne-Rutherford [25] balance; McLaughlin [15], with Tobolsky, has used the Schaevitz transformer discussed in [31]. All of these devices use a commercially available instrument to record force automatically. Other units that can be used in investigations of this type include the Sookne-Rutherford apparatus [25] and the Sookne-Harris modification thereof†; the Reichardt-Schaevitz-Dillon stress-strain-time apparatus [21]; the Ballou apparatus [3]; and the commercially available unit of the Instron Engineering Corporation.‡ These latter instruments are ordinarily used in short-time stress-strain experiments but, with proper precautions, are suitable for stress-relaxation experiments at constant strain over periods of some minutes or even hours.

Owing to the length of time involved (approximately 3 days) in carrying out a single stress-relaxation experiment at constant strain, it was felt that it would be profitable to design and build a multi-unit autographic stress-relaxometer of at least six units, and thereby be enabled to carry out experiments simultaneously. The instrument was designed along the lines of the *LVDT* ring-dynamometer apparatus described by Stein and Schaevitz [31], and by Reichardt, Schaevitz, and Dillon [21]. The essential differences in the electrical systems are the use of a modified Brown multipoint recording potentiometer, and the elimination of the mechanism which maintains constant elongation.

A diagram of the ring dynamometer *LVDT* strain gage assembly is shown in Figure 1. Most of the metal parts are made of aluminum or brass to prevent disturbance in the magnetic field of the transformer. The ring dynamometer, *A*, was designed so that the movement caused by the decrease in load during the course of the experiment was negligible. The change in the diameter of the ring was approximately 0.003 cm. per gram of load. Since the samples selected were 8 to 10 cm. in length, and the loads produced on extension of the material were in the range 2–5 g., the movement of the ring and its ef-

* Statham Laboratories, Inc., Beverly Hills, Calif.
† Harris Research Laboratories, Washington, D. C.
‡ Instron Engineering Corp., Quincy, Mass.

fect upon the constant elongation requirements of this technique was $2\text{–}5 \times 0.003/10 \sim 0.1\%$.

The principle involved in the operation of the strain gage is straightforward. When a load is applied to hook *B*, a displacement, linear with load, is transmitted by the ring dynamometer, *A*, to the iron core, *C*, moving within the linear variable differential transformer (*LVDT*), *D*. The two secondaries of the *LVDT* (Figure 2) are connected in series opposition so that when the iron core is centrally located within the transformer, the voltages from the secondaries cancel and there is no output signal. If the core is moved from this position as a result of the application of a load, a voltage is produced whose magnitude depends linearly upon the distance the core is displaced from the null position, and whose phase depends upon the direction of displacement.

A circuit with two *LVDT's* arranged in bridge arms (see reference [21]) is shown in Figure 2. It contains a recording potentiometer modified by removing parts of the conventional D.C. bridge circuit and replacing them with an *LVDT* mounted as shown in Figure 3. The converter in the Brown recorder amplifier was replaced by a suitable input transformer to accommodate the 60-cycle signal fed from the *LVDT* bridge. The use of an *LVDT* bridge circuit and the modified amplifier has a twofold advantage: first, it eliminates to a large extent the dependence of the output signal upon the line voltage; second, it obviates the difficulties involved in stable linear rectification of a low-level 60-c.p.s. signal.

The sequence of operations is as follows. A load placed on hook *B* (Figure 1) produces a displacement of the core *C* as a result of deformation of the ring *A*. An unbalance signal occurs in the bridge circuit formed by the strain gage *LVDT* and the recorder *LVDT* (Figure 2). This signal is fed into an amplifier through a shielded coaxial cable. The output of the amplifier drives a synchronous motor, which in turn drives the micrometer screw (Figure 3) of the recorder *LVDT* assembly, and positions the printing mechanism of the recorder. The micrometer screw moves the iron core of the recorder *LVDT* until the signal produced by this transformer

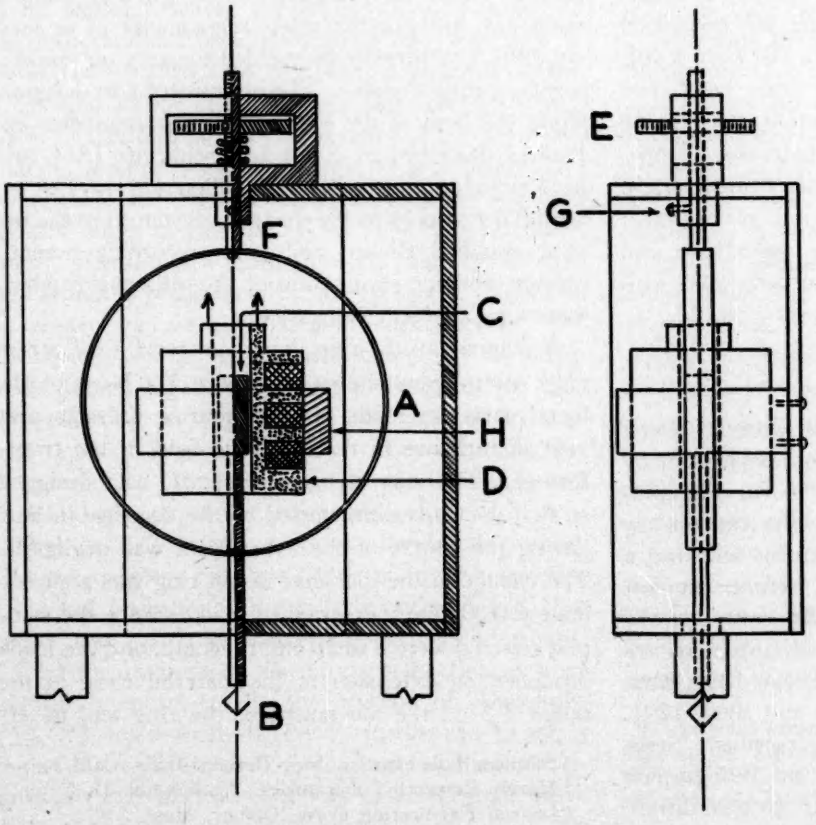

FIG. 1. *Ring dynamometer and linear variable differential transformer strain-gage assembly. Letters designate items described in the text.*

cancels that of the strain gage *LVDT* at some null point. The amplifier then receives zero signal, the motor stops, and the printing mechanism records the position of the null point. A multipoint recorder permits several experiments to be carried out simultaneously, the recorder channel selector switch merely taking the output of each unit in turn. The recorder used in the present apparatus can accommodate twelve separate channels, but since only six relaxometer units were built, the remaining stations were connected in parallel so that two recording channels were available for each unit.

A number of instrumental difficulties were encountered in making the apparatus sufficiently stable for use in long-term stress-relaxation experiments. Although in none of the papers cited previously where an *LVDT* was used as the stress-measuring device was there noted any instability of the output of the system over extended periods of time, it was found in the present apparatus that there was a complicated and appreciable dependence of the record upon room temperature fluctuations. A short-time fluctuation arose from changes in ring diameter and, consequently, in core position, due to thermal expansion. A second source of temperature dependence

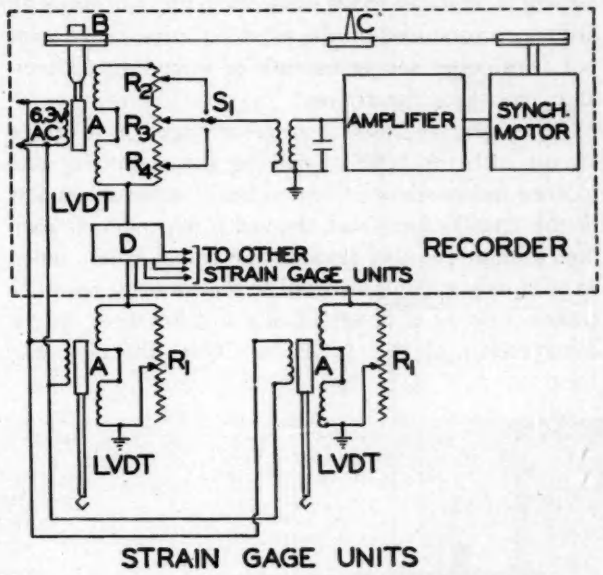

FIG. 2. *Block diagram showing arrangement of linear variable differential transformers and mode of operation of the apparatus.* A—*Linear variable differential transformer and core.* B—*Circular drum mounted on a micrometer screw driven by synchronous motor. The micrometer screw moves the core of the recorder* LVDT. C—*Schematic representation of printing mechanism, which rides on violin string driving* B. D—*Recorder selector switch which connects in turn each of the strain gage* LVDT*'s to the recorder* LVDT. $R_{1, 2, 3, 4}$—*Resistors whose function is described in the text.*

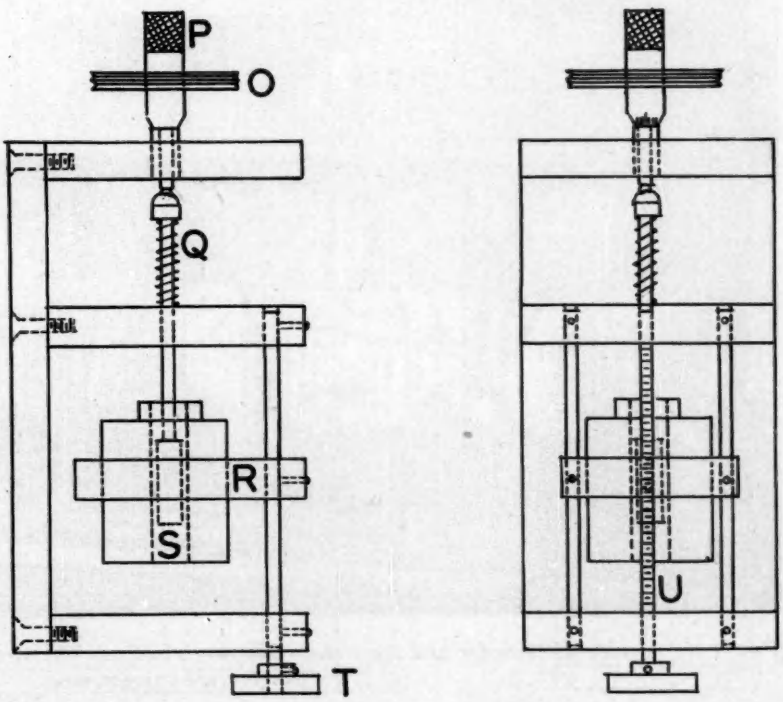

FIG. 3. *Recorder linear variable differential transformer assembly.* O—*Drum driven by synchronous motor.* P—*Micrometer screw.* Q—*Spring-loaded shaft attached to the micrometer screw by means of a steel ball used as a thrust bearing.* R—*Aluminum yoke supporting linear variable transformer.* S—*Iron core of* LVDT. T—*Zero-adjust knob for moving* LVDT *with respect to iron core by means of threaded shaft passing through yoke.* U—*Threaded shaft passing through* LVDT *yoke.*

was traced to the expansion and contraction of the more massive parts of the strain gage assembly mounting. This effect is much slower than that attributable to the ring dynamometer, and is in the opposite direction. It was found that control of ambient temperature about the gage within approximately 0.5°C eliminated the fluctuations in the record almost completely. Some hunting was observed as a result of the ambient temperature fluctuations resulting from delay in the control circuit, but the oscillations so produced on the most sensitive range were not considered severe enough to introduce appreciable error into the record.

Although the *LVDT's* were arranged in a bridge circuit with the hope of making the sensitivity and balance independent of line voltage variations, a few of the transformers still showed a dependence upon line voltage, possibly because the transformers failed to be closely enough matched to the common recorder transformer as a result of slight differences in the construction of the *LVDT*'s. This difficulty was corrected by installing a line-voltage regulator. Disturbances from stray fields were minimized by utilizing shielded cables and placing any possible sources of disturbing fields as far from the units and leads as was practical. The transformers, including the cores, were supplied by Schaevitz Engineering.* The cores were found unsuitable until they were quenched in water from a red heat and then aged for some weeks. When the foregoing precautions were observed, it was found that stability within 0.5% of full scale could be obtained on three ranges over a period of 4 days.

The assembly of six units and recorder is shown in Figure 4. A complete single unit is shown in Figure 5. The sample is stretched by lowering the platform *I* the required amount, as indicated upon the scale, *J*, by the hairline indicator, *K*. The scale can be read to 0.005 in. The platform is lowered manually by rotating knob *L*, which drives screw *M*. The platform supports a water-jacketed container,

* Schaevitz Engineering, Pennsauken Township, Camden, N. J.

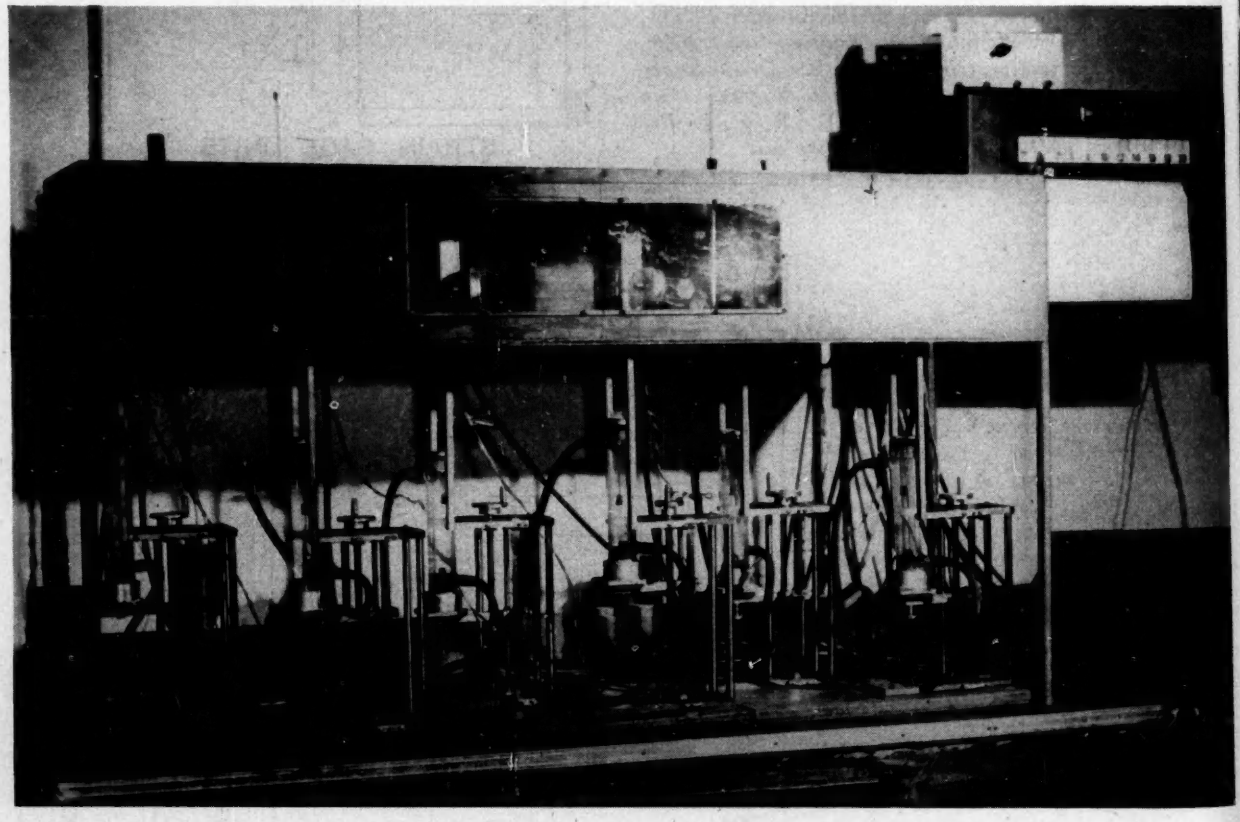

FIG. 4. *Assembly of recorder and six stress-relaxometer units. The strain-gage units are enclosed in a constant temperature compartment.*

N, in which the sample is mounted between two Phosphor-bronze clamps (not shown in the figure). The lower clamp is attached to a brass cylinder by a setscrew. The cylinder fits snugly into the central reaction chamber, and is heavy enough to keep the lower clamp immobile during the extending of the sample and the course of the experiment. The upper clamp is soldered to a stiff Nichrome wire (B & S gage No. 22) fashioned with a hook on one end suitable for attachment to the strain gage assembly. This small size of wire was used to decrease the effect of change in hook buoyancy caused by evaporation of liquid from the reaction chamber during the experiment. To decrease the rate of solution evaporation, the reaction chamber was covered with a Lucite plate containing a small hole, through which the Nichrome wire passed freely. In order to minimize the possibility of catalytic effects, the entire reaction chamber metal assembly (clamps, weight, and hook) was plated with rhodium over a nickel

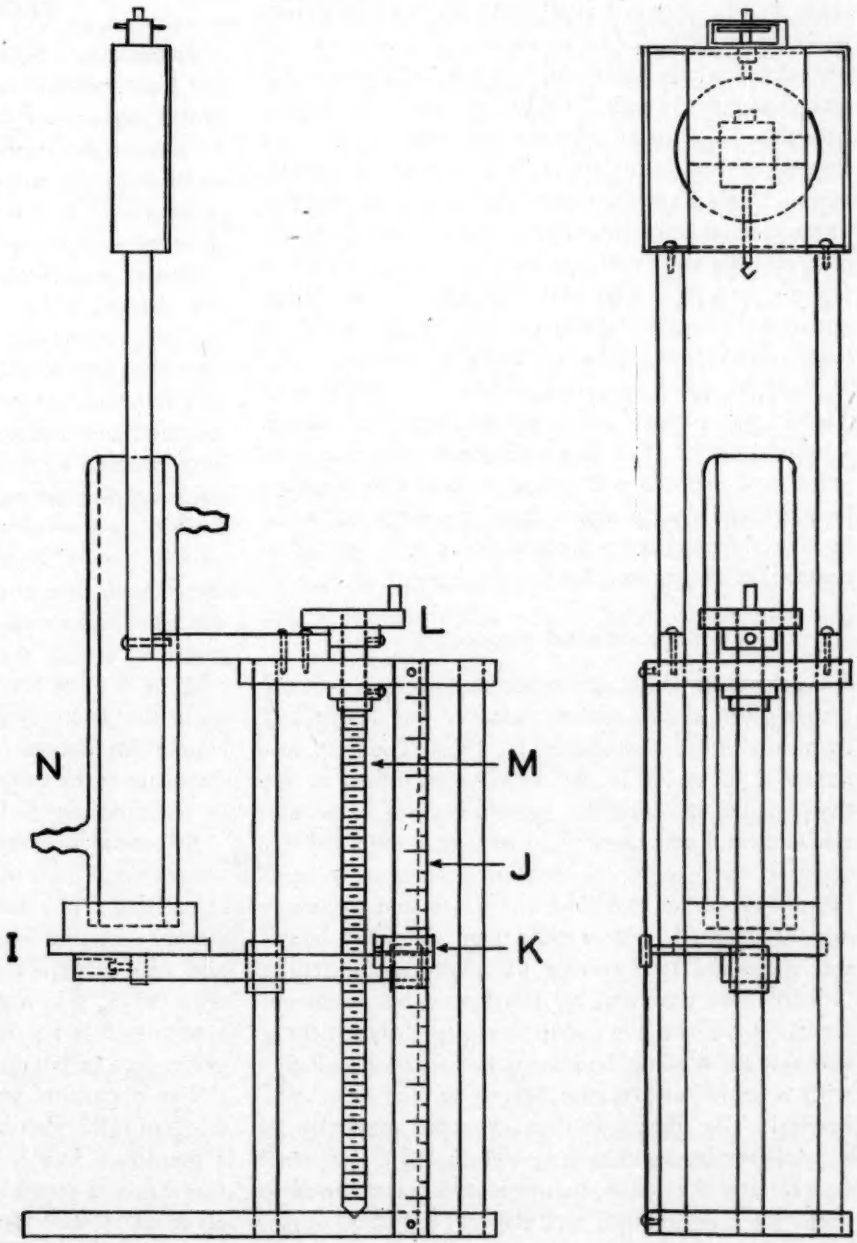

FIG. 5. *Complete single stress-relaxometer unit. Letters are explained in the text.*

undercoat. Water was circulated through the outer jacket of container N from a constant temperature bath by a pump (not shown in the figure). The temperature of the reaction chambers was thereby maintained to within ± 0.1°C.

Calibration

With resistors R_1, R_2, R_3, and R_4 (Figure 2) set approximately in the middle of their range, and with zero load on the dynamometer, the thumb screw, E (Figure 1), attached to the ring dynamometer by shaft F was adjusted until the core was in a null position, as indicated by absence of zero shift on the recorder pen when the range switch, S_1 (Figure 2), was changed through the 10-, 5-, and 2-g. ranges. Setscrew G (Figure 1) was tightened to prevent slipping of the shaft during the course of the experiment. A load appropriate to the range was attached to the unit, and the instrument was calibrated for the correct scale deflection on each range by adjusting R_2, R_3, and R_4. The same procedure was carried out with the remaining instruments, except that these units were calibrated by adjusting R_1 instead of R_2, R_3, and R_4, since the latter resistors are common to all the transformers through the recorder channel selector switch. For this calibration procedure, all units, and especially the ring dynamometers, must be machined nearly alike, since any large variation in ring dynamometer characteristics will not allow calibration of that unit by the adjustment of R_1.

Experimental Procedure

At the start of the experiment a fiber was selected from a given sample, and its diameter was determined by means of the vibroscope [10, 18]. The fiber was mounted in water in the reaction chamber at the temperature at which the experiment was to be carried out, and was allowed to remain unextended for a period of 24 to 36 hrs. to allow it to come to equilibrium so far as swelling and associated processes were concerned. After this time, the fiber length was measured by lowering the platform until fiber "crimp" was removed, as determined by visual observation. Since the clamp-to-clamp distance for a given scale reading had been measured previously with a cathetometer, the length of the fiber was known. The fiber was then extended manually by a predetermined amount (generally 15% for wool fibers), and the stress thus produced was allowed to decay for a period of 1 or 2 days (1400–2800 min.). After the desired length of time elapsed, the water was siphoned off from the reaction chamber, and a solution of the reagent whose action on the fiber was to be studied was introduced. After the record had been taken over a sufficient time for the reaction to approach or reach completion, the clamp assembly was removed and thoroughly rinsed. The reaction chamber was scrubbed clean, and rinsed with a liberal quantity of tap water to remove traces of the cleanser. The chamber was finally rinsed with distilled water.

Preliminary Results

Three basic assumptions are involved in the design and interpretation of the experiments to be reported in this paper: (*1*) the rupture of cross-links controls the stress-relaxation behavior of the fiber at constant strain; (*2*) all cross-links in the system behave independently; (3) the reagents used are specific for a given type of bond.

Water is active in breaking hydrogen bonds, and can also enter into the hydrolytic decomposition of the —S—S— bond of cystine [16, 23, 24, 27, 37]. The first part of the stress relaxation in water may be attributed to the rupture of hydrogen bonds. At longer times and higher temperatures the hydrolytic rupture of the cystine bond probably controls the relaxation processes. After the hydrogen bonds that are in stress-supporting positions have been removed, the —S—S— bonds support most of the stress with lesser contributions from salt bridges, chain entanglements, and crystalline regions. If the reaction between the —S—S— bond and a reducing reagent is to be studied, there must be chosen a reagent that has only minor effects on the other stress-supporting bonds. Then the decay of stress produced upon the addition of the reducing agent should be an indicator of the way the reaction proceeds.

Experiments were carried out: (*1*) to determine the stability of the apparatus under conditions of constant load; (*2*) to compare the data obtained in stress-relaxation experiments with previous work; and (*3*) to explore the effects of various reagents upon wool, silk, and nylon in order to test the assumption that the reagents chosen are specific for a given type of bond.

The apparatus was found to be stable to within 0.5% of full scale on the 2-, 5-, and 10-g. ranges over a period of 5 or 6 days. Since the recorder chart was run at a speed of 6 in./hr. to conserve paper, an error of ± 0.2 min. was found, and this interval

may not be negligible during the first minute of the experiment. The apparatus was not tested for longer periods of time, since experiments of longer duration were not planned.

Figure 6 gives the results for stress-relaxation experiments under conditions similar to those used by the previous workers Katz and Tobolsky [12]. Here the relative force, f/f_{60} (force normalized to the force at 60 min. after the start of the extension), is plotted against the logarithm of time in minutes. The force at 60 min. was chosen as the reference force for several reasons: (*1*) the effect of different rates of extension has disappeared; (*2*) the rate of change of force is small by this time; (*3*) this method of plotting removes some of the effect of fiber size; and (*4*) this choice of plotting has been made by the previous authors. The same sample of wool keratin (Columbia 56's) was used, and the same conditions of extension and temperature (15%, 50°C) were maintained. It is seen from Figure 6 that the present results seem to show a greater degree of reproducibility than those of Katz and Tobolsky. A possible explanation may be that in the present investigation an attempt was made to select fibers with comparable cross-sectional areas (approximately $1000\mu^2$), and to avoid the use of fibers of nonuniform diameter, as observable with the naked eye. As in the experiments of Katz and Tobolsky, the rate of extension of the sample could not be controlled carefully since a manual extension apparatus was involved. An investigation was carried out to determine roughly the influence of the rate of extension upon the rate of stress relaxation. These experiments indicated that different rates of extension have little effect upon the rate of stress relaxation if the zero time for the process is taken at the beginning of the relaxation. In the experiments reported here, zero time is taken for convenience at the beginning of the extension of the sample, and hence some lack of reproducibility should be expected. At longer times, however, the differences in extension rates would not be expected to be reflected strongly in the relaxation processes.

In experiments reported earlier the relative force was plotted, rather than the stress, in order to obviate the tedious determination of cross-sectional areas. It was believed that, in so far as stress-relaxation behavior was concerned, fibrous materials were uniform from fiber to fiber, and that samples would show uniform behavior when reduced to unit cross-sectional area. However, when the areas are measured, as in the present experiments, a fiber-to-fiber variation is found to exist when the actual stress is plotted against time. Figure 7, based on the same experiments as Figure 6, shows the relaxation behavior for the actual stress. It is seen that the relative force behavior, as given in Figure 6, is more reproducible from fiber to fiber than the actual stress behavior, as given in Figure 7. The source of this difference in reproducibility has not yet been established.

A series of experiments was carried out in order to determine the effect of various reagents upon the stress-relaxation behavior of wool (Columbia 56's), silk, and nylon. The experimental procedure was as

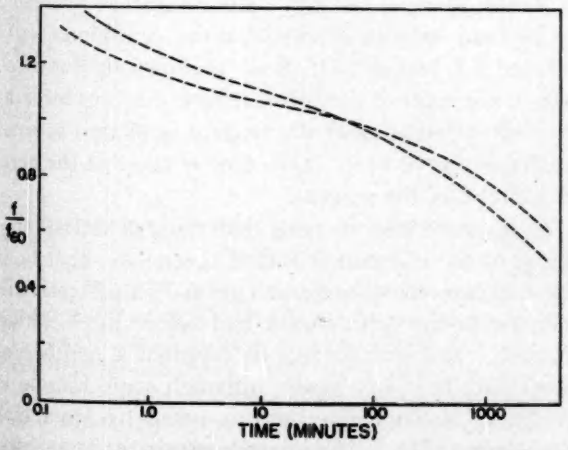

FIG. 6. *Limits within which lie stress-relaxation curves for six Columbia 56's wool fibers in water at 50°C and 15% extension. Here relative force is plotted against time (min.) on a logarithmic scale.*

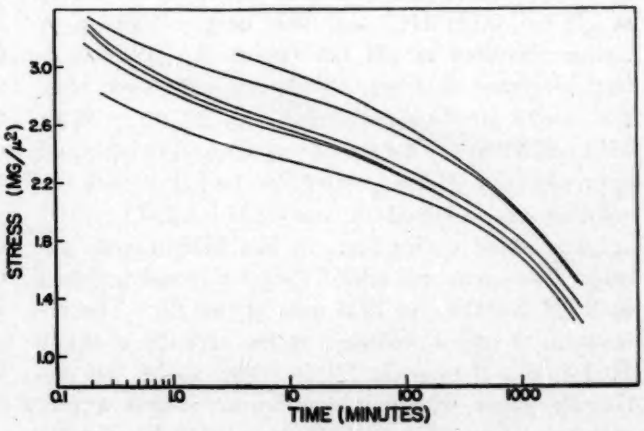

FIG. 7. *Stress relaxation of six Columbia 56's wool fibers in water at 50°C and 15% extension (same original data as Figure 6). Stress (mg./μ^2) is plotted against time (min.) on a logarithmic scale.*

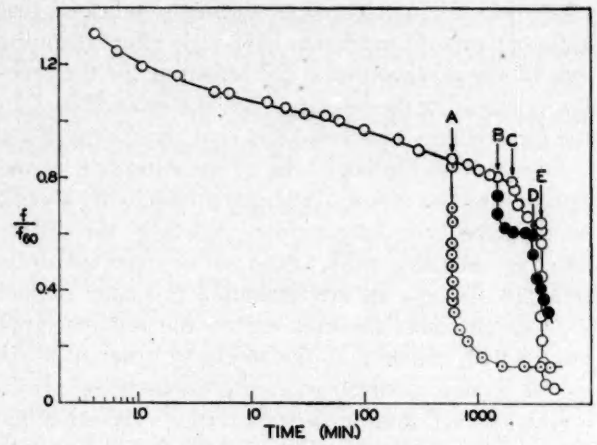

FIG. 8. *Stress relaxation of Columbia 56's wool fibers under the action of various chemical agents at 30°C and 15% extension. Relative force is plotted against time (min.) on a logarithmic scale.* A—*Addition of 0.1*M *soduim bisulfite at pH 6.5.* B—*Addition of 0.1*M *hydrochloric acid.* C—*Addition of 10*M *urea.* D—*Addition of 0.1*M *sodium bisulfite at pH 1.2.* E—*Addition of 0.1*M *sodium bisulfite in 10*M *urea.*

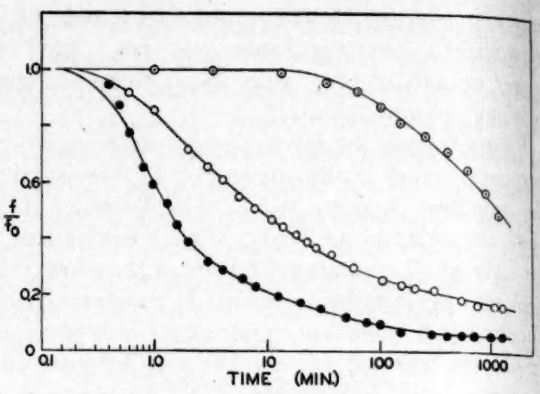

FIG. 9. *The stress relaxation of Columbia 56's wool fibers at 30°C and 15% extension under the action of 0.1*M *sodium bisulfite at a variety of conditions. Here the stress relative to the stress at the time of addition of the reagent is plotted against the time (min.) on a logarithmic scale. The solid circles show the action of sodium bisulfite dissolved in 10*M *urea, the open circles that of sodium bisulfite at pH 6.5, and the dotted circles that of sodium bisulfite at pH 1.2.*

described above. Figure 8 shows the stress decay, f/f_{60}, for three samples of wool keratin in water at 30°C and 15% extension. The samples were conditioned in water at 30°C for 24 hrs. prior to extension. The stress produced on extension of the fiber was allowed to decay in water for various periods of time before reagents were added. Each experiment was carried out with a different fiber, and the initial portion of the curve (open circles to point *C*) represents the average behavior of three fibers relaxing in water. The reagents added were 0.1*M* $NaHSO_3$ at pH 6.5, 0.1*M* HCl, and 10*M* urea. Addition of sodium bisulfite at pH 6.5 (point *A*) produces a large decrease of stress, a finding in agreement with the results previously reported [12, 20, 26]. With HCl (added at *B*) the stress was allowed to relax for approximately 24 hrs. After this period of time the solution was siphoned off, and 0.1*M* $NaHSO_3$ at pH 1.2 was added (point *D*). In like fashion, with another fiber, urea was added (point *C*), and replaced by 0.1*M* $NaHSO_3$ in 10*M* urea (point *E*). The relaxation of stress produced by the addition of 0.1*M* HCl (point *B* to point *D*) is rather slight, but extremely rapid, reaching equilibrium within a few minutes. The action of 10*M* urea (*C* to *E*) is comparatively slow, equilibrium not being reached within 24 hrs. After the fiber has been allowed to relax in acid for about 1 day, the addition of a sodium bisulfite solution adjusted to pH 1.2 (point *D*) causes an additional relaxation which is much slower than that at pH 6.5. This behavior may be due to the effect of pH on the concentration of the bisulfite ion. At pH 1.2 and 6.5 the odor of sulfur dioxide is detected above the solution, but it is believed that any decrease in concentration from this source is unimportant in this experiment. The additional relaxation produced by a solution of 0.1*M* $NaHSO_3$ in 10*M* urea (following point *E*) is more rapid than that produced by $NaHSO_3$ alone at pH 6.5. The relaxation produced by sodium bisulfite under various conditions (pH 6.5 and 1.2, and in 10*M* urea) is shown in Figure 9, where the ratio of the force at time *t* to the force at the time of addition of the reagent is plotted against the logarithm of time. Zero time is taken at the time of addition of the reagent.

It is interesting to note that the relaxation produced on the addition of acid is reversible—that is, if the acid is replaced by water (pH 6–7) the stress will increase to the value that it had before the addition of acid. This process can be repeated a number of times with the same result, although some fatigue is evident. Similar behavior was noted by Ripa and Speakman [22] in their stress-strain experiments. This "acid effect" on stress relaxation is observed to be not nearly so great with hair keratin [20] as with wool keratin. Moreover, the swelling effect of 0.1*M*

HCl is small, hair being swollen about 3% [4] and wool about 6% [19] by this reagent. If the decay of stress produced by the addition of acid of this concentration is to be explained in terms of swelling of the fiber, then stress relaxation must be very sensitive to swelling. Cacella [7] has found that H_2SO_4 is very difficult to wash out of the fiber, a result indicating that some of the acid is strongly bound in keratin. In view of the reversibility of the stress-relaxation behavior of wool keratin treated by HCl, it must be concluded that not all of the acid adsorbed by the fiber is effective in rupturing cross-links. A similar, though slower, relaxation of stress produced by neutral salts (0.1 to 1.0*M* NaCl) [12, 13] probably does not stem from the same cause, since dilute solutions of neutral salts do not affect the stress-strain behavior of wool keratin [6], nor do they cause appreciable swelling [36]. It may be that the effect of salts is similar to that of the strongly bound acid mentioned above.

A possible explanation of the behavior with hydrochloric acid as reported here and as observed by Ripa and Speakman [22] is that acid-sensitive bonds (possibly salt bridges) [28] occurring along the same peptide chain produce small loops in the chain. When these bonds are broken by the addition of acid, these "loops" are opened and a decay of stress is observed. When the acid is removed and replaced by water, the forces between the groups that enter into the formation of these acid-sensitive bonds are strong enough for them to re-form. This interpretation implies that the groups involved are in neighboring positions along the peptide chain, that the molecular rearrangement (which produces the observed changes in physical properties) is merely the folding and unfolding of the chain, and that the reaction involving the scission of these bonds is reversible, the position of the equilibrium being dependent upon pH. If the molecular rearrangement that follows the rupture of these bonds is not restricted in some way, a reversible process would probably not be observed. It is to be noted that the decrease of relative force accompanying the addition of acid is relatively small when compared to the action of bisulfite, a fact possibly indicating that the contribution of these bonds to stress support is not great. This conclusion is in agreement with the work of Consden *et al.* on keratin hydrolyzates [8].

If the acid-sensitive bonds can be identified with the salt bridges, one is tempted to explain the stress-relaxation behavior produced by neutral salts in terms of a formation of an ion cloud between the charged amino and carboxylic groups, with consequent decrease of the attractive forces between them. The action of dilute (approximately 0.1*M*) salt solutions would be expected to be somewhat slower than that produced by acids, since many more ions would be involved in the formation of an ionic cloud. How-

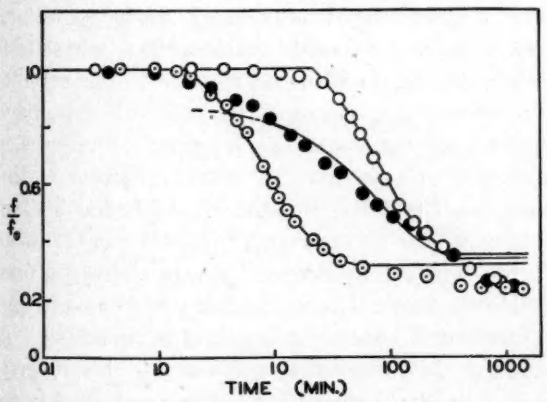

FIG. 10. *The stress relaxation of Columbia 56's wool fibers at 50°C and 15% extension under the action of 0.01*M *sodium bisulfite, 0.01*M *cysteine, and 0.01*M *thioglycolic acid, all at pH 6.5. The stress is plotted in terms of the stress at the time of addition of reagent. The solid circles show the action of sodium bisulfite, the dotted circles that of cysteine, and the open circles that of thioglycolic acid. The solid lines are calculated exponential curves, adjusted to take into account a preliminary time delay.*

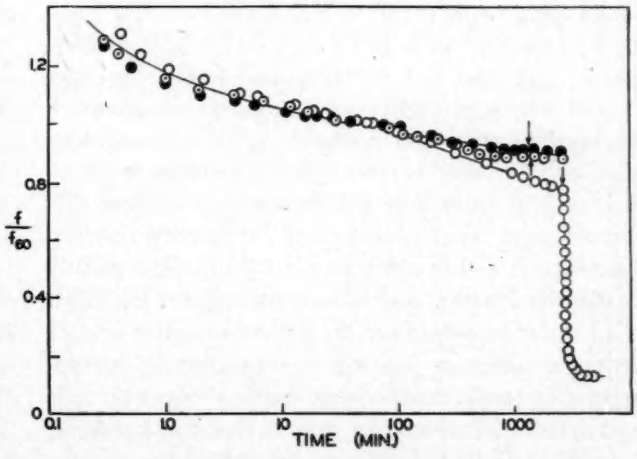

FIG. 11. *The stress relaxation of wool (open circles), silk (dotted circles), and nylon (solid circles) in water and 0.1*M *sodium bisulfite at 30°C. The arrows show the point of addition of sodium bisulfite.*

ever, it is difficult without further *ad hoc* assumptions to reconcile the absence of effects of dilute neutral salt solutions on the stress-strain and swelling properties of keratin fibers with this mechanism.

Figure 10 shows the effect of the reducing reagents —cysteine and thioglycolic acid (as well as sodium bisulfite)—on the stress relaxation of wool fibers at 50°C and 15% extension. Zero time is taken at the time of addition of the reagent, and the force is normalized to the force at zero time. The reagents (0.01*M*) were adjusted to pH 6.5 before they were added to the fiber in the reaction chamber. The fibers were previously relaxed in water for about 2400 min. The solid lines in this figure were calculated from an exponential decay law:

$$f/f_o = e^{-k_o t} + \text{const.},$$

where k_o is a rate constant. It is seen that the action of cysteine is more rapid than that of sodium bisulfite or thioglycolic acid. The stress relaxation produced by cysteine and by thioglycolic acid follows the exponential rather well. The relaxation for sodium bisulfite, on the other hand, is not exponential in form, and indicates that the mechanism for the relaxation is complicated by other effects. A possible explanation for this behavior may be found in terms of the salt effects and cross-linking reactions, accompanied by interference of hydrogen bonds in the process. The fact that the curve for a fiber which has been relaxed in water and treated with 10*M* urea followed by 0.1*M* $NaHSO_3$ in 10 *M* urea follows an exponential more closely than does a fiber relaxed only in water and then in 0.1*M* $NaHSO_3$ at pH 6.5 indicates that hydrogen bonds affect the relaxation (see Figure 7). It remains to be seen whether the salt effect contributes significantly to the relaxation produced by bisulfite and other reducing agents. In connection with the reaction of keratin with sodium bisulfite, it is of interest to note that human hair behaves differently from wool, inasmuch as the reaction between hair keratin and bisulfite was found to follow pseudo first-order kinetics, and to be complete in 1 hr. [20].

In order to determine the effects of water and of reducing reagents on different materials, stress-relaxation experiments were carried out with silk and nylon. Silk resembles wool in that it is a protein, but differs in that it contains no cystine and is relatively free of ionizable amino and carboxylic groups and bulky side-chains. Nylon, a polyamide, although quite different chemically from wool and silk, would be expected to show a similar type of hydrogen bonding. The results given in Figure 11 show that silk, wool, and nylon under comparable conditions have the same type of stress-relaxation behavior for that period of time where hydrogen bonds are believed to control the relaxation processes. The reducing agents used in these investigations have no effect upon the stress-relaxation behavior of silk and nylon, but, as noted previously, drastically affect the rate of stress decay of wool keratin. This difference in behavior is attributed to the presence of the cystine disulfide bond in the latter material and its contribution to stress support.

Finally, stress decay in water as a function of extension was studied for all the materials concerned in these investigations. The most extensible material, wool, was studied at elongations up to 20%. Within this range, the stress-relaxation behavior was found to be independent of the degree of extension. The same result was found for nylon at extensions up to 15% and for silk up to 10%.

Summary

A description of the apparatus used in the stress-relaxation experiments is presented. With this apparatus six stress-relaxation experiments on fibrous materials may be carried out simultaneously. The device utilizes ring-dynamometer strain gages and linear variable differential transformers, whose outputs are fed into a multipoint recorder. The stability of the apparatus is discussed, and the calibration and experimental procedures are described. Preliminary results are presented on the effect of urea, hydrochloric acid, cysteine, thioglycolic acid, and sodium bisulfite on the stress-relaxation behavior of wool keratin. The rate of stress decay produced by urea is relatively slow. The stress decay produced by hydrochloric acid occurs rapidly, and is reversible. A mechanism is presented to account for this reversibility. The stress-relaxation behavior of wool keratin in cysteine and thioglycolic acid solutions is exponential in character, but that in sodium bisulfite is not. It is shown that the stress-relaxation behavior of silk, wool, and nylon in water under comparable conditions is very similar, and that sodium bisulfite does not affect silk and nylon, whereas it drastically changes the stress-relaxation behavior of wool keratin, presumably because of its action on the disulfide bonds.

Acknowledgment

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II. Kinetics of the Reduction of Wool Keratin by Cysteine

E. T. Kubu and D. J. Montgomery

Abstract

The kinetics of the reaction of cysteine solutions with wool keratin was studied as a function of concentration, hydrogen ion concentration, and temperature by means of the stress-relaxation technique. The reaction was found to follow pseudo first-order kinetics when the cysteine was present in sufficient excess to maintain its concentration constant during the reaction. The kinetics of the process is discussed in terms of the scission of the disulfide cross-links in keratin.

Introduction

In Part I of this report it was found that the stress-relaxation behavior of wool keratin (Columbia 56's) held at constant strain followed a law exponential in time when the fiber was treated with certain reducing agents. Part II extends the studies of the reaction between cysteine and wool keratin, and attempts a quantitative interpretation of the behavior observed. The apparatus used in the experiments reported here was described in Part I.

Theory

The reduction of cystine in keratin by cysteine is an example of a process that can be investigated with comparative ease by stress-relaxation techniques, but only with difficulty by conventional means. In a stress-relaxation investigation, there are the limitations that only those bonds which support stress can be studied, and that only the bond-breaking action of the reagent can be determined. Information is not obtained directly about those bonds that do not support stress, nor about the products of the reactions. Considering the reaction of cysteine with cystine in keratin,* one can expect to tell only when some bond in the chain R—S—S—R is broken by reaction with Cys—SH (or, indeed, with any other reactant that happens to be present); information cannot be obtained on subsequent reaction of the chain fragments.

It is likely, in view of the work of Bersin and Steudel [1] on the reaction between cystine and thioglycolic acid, that the reaction between cystine and cysteine goes predominantly according to the following scheme:

$$\mathrm{R{-}S{-}S{-}R + Cys{-}SH \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R{-}S{-}S{-}Cys + R{-}SH,} \quad (1a)$$

$$\mathrm{R{-}S{-}S{-}Cys + Cys{-}SH \underset{k_4}{\overset{k_3}{\rightleftharpoons}} Cys{-}S{-}S{-}Cys + R{-}SH.} \quad (1b)$$

It would be expected that this pair of successive bimolecular reactions is much more likely than the single trimolecular reaction

$$\mathrm{R{-}S{-}S{-}R + 2\,Cys{-}SH \underset{k_6}{\overset{k_5}{\rightleftharpoons}} Cys{-}S{-}S{-}Cys + 2R{-}SH.} \quad (2)$$

The experimental evidence to be presented later in this paper shows that the reaction actually does follow (1*a*) and (1*b*).

In the usual way, differential equations can be derived for the rate of disappearance of cystine according to either of the schemes indicated above, but the resulting equations are not very useful in the general case because of their mathematical intractability. Fortunately, in the stress-relaxation experiments under consideration it is possible to make the simplifying assumptions (*1*) that reverse reactions (cross-linkings) occur in such fashion that bonds are formed in stress-free positions only and therefore do not affect the stress decay, and (*2*) that the concentration of reducing reagent is esssentially constant at the initial concentration $[\mathrm{CysSH}]_o$ throughout the course of the experiment. Under

* The notation in this article is Cys—SH = free cysteine, and R—S—S—R = cystine bound in keratin.

these circumstances the rate of disappearance of cystine according to scheme (1*a*, 1*b*) is given by

$$-d[\text{RSSR}]/dt = k_o[\text{RSSR}] = k_1[\text{RSSR}][\text{CysSH}]_o. \quad (3)$$

Because not all the stress is supported by cystine bonds that can be attacked by cysteine there will be a stress $\sigma(\infty)$ remaining at long times. Hence, to identify the rate of bond scission with rate of stress decay, the additional assumption must be made that only the difference between the observed stress $\sigma(t)$ at time t and this final stress, $\sigma(\infty)$, will be proportional to the cystine concentration:

$$[\sigma(t) - \sigma(\infty)] \propto [\text{RSSR}]. \quad (4)$$

Since the fiber cross-sectional area is constant under the conditions of the experiment, the stress is proportional to the measured force $f(t)$, and equation (4) becomes

$$\frac{f(t) - f(\infty)}{f(0) - f(\infty)} = \frac{[\text{RSSR}]}{[\text{RSSR}]_o}, \quad (5)$$

where $[\text{RSSR}]_o$ represents the concentration of disulfide bonds at the start of the experiment. Integration after substitution of equation (3) in equation (5) gives

$$\frac{f(t) - f(\infty)}{f(0)} = \left[1 - \frac{f(\infty)}{f(0)}\right] \exp(-k_1[\text{CysSH}]_o t). \quad (6)$$

The experimental data for fibers relaxed at a fixed cysteine concentration can be tested to see whether the time variation follows the exponential law of equation (6). If this form of law is satisfied, the dependence of the rate constant upon cysteine concentration will determine the choice of mechanism between (1*a*, 1*b*) and (2).

Experimental Procedure

The technique and apparatus described previously (Part I) were used. The diameter of each wool fiber (Columbia 56's) was determined by means of the vibroscope [7, 11]. The fibers were mounted in the reaction chamber, which was filled with water at a specified temperature, and were allowed to rest in an unstrained condition for a period of 24–36 hrs. The fibers were then stretched to 15% extension, and the stress produced thereby was allowed to decay for approximately 48 hrs. After this time, the water was siphoned off and replaced by cysteine solution. The additional stress decay produced by the cysteine was followed for about 24 hrs. In those experiments where relaxation in cysteine solutions was carried out at pH values other than 6.5, the fiber was relaxed in acid (HCl) at the desired pH before the addition of cysteine.

The cysteine solution was made up from cysteine hydrochloride prior to each experiment. The pH was adjusted, by addition of sodium hydroxide or hydrochloric acid, to the desired value, as measured with a Beckman Model G glass-electrode pH meter. The cysteine hydrochloride, obtained from the Fisher Scientific Company, contained 98%–99% reagent by weight, the remainder consisting presumably of water. The cysteine concentration was determined by adding an excess of iodine, and back-titrating with standard sodium thiosulfate solution [10].

In all the experiments discussed in this paper, zero time is taken as the time of adding cysteine solution, and all force measurements are normalized to the force at zero time. A logarithmic time scale and a linear relative force scale have been chosen for convenience. Since the data were recorded automatically with the Brown Multipoint Recording Potentiometer described earlier (Part I), the plots of the experimental results should be continuous curves. However, continuous lines will usually represent theoretical curves, and the experimental data are plotted as points taken at convenient intervals from the recorder chart.

Results and Discussion

Figure 1 is a typical plot of the stress decay as a function of time for single wool fibers at 50°C and 15% extension in different concentrations of cysteine at pH 6.5 The stress had decayed previously in water for 48 hrs. (2880 min.). The circles represent points taken from the recorder chart, and the solid lines show exponentials fitted to the data. The theoretical curves have been shifted slightly to take into account an induction period attributed to diffusion of the reagent into the fiber [8]. This shift involves the subtraction of a constant time interval from the argument of the exponential. The correlation between the time delay and the cross-sectional area of the fiber seems to indicate that diffiusion is the controlling phenomenon at short times. However, the delay was usually so small that the uncertainties in the experimental curves precluded a quantitative analysis of the process.

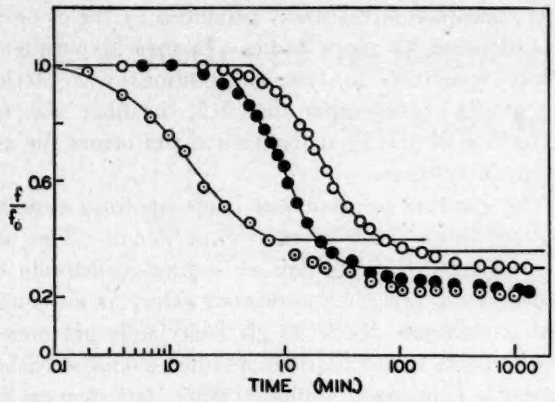

FIG. 1. *Stress relaxation of Columbia 56's wool fibers at 50°C and 15% extension with different concentrations of cysteine at pH 6.5. The dotted circles represent data for 0.044M cysteine, the solid circles 0.011M cysteine, the open circles 0.005M cysteine. The solid lines represent exponentials fitted to the data.*

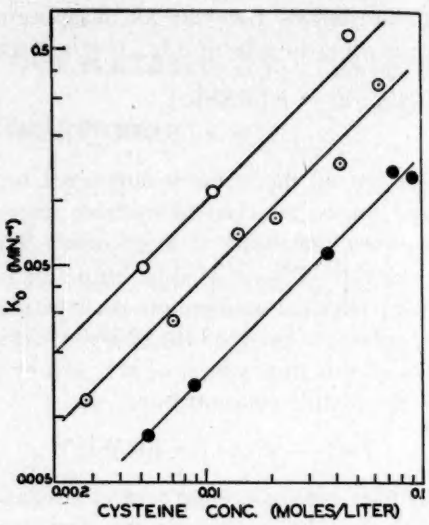

FIG. 2. *The plot of the observed rate constant, k_0, as a function of cysteine concentration. Logarithmic scales are used for both coordinates. The open circles represent data at 50°C, the dotted circles data at 42°C, and the solid circles data at 30°C.*

It will be noted that at very long times the relative force does not approach zero, nor does it follow the exponential describing the major portion of the stress relaxation. The failure of the stress to reach zero may be due to the existence of "crystalline"—that is, highly ordered—regions that support stress. The deviation from the theoretical curves may be due to the presence of some less reactive cystine bonds, to the existence of a "salt effect" similar to that reported by Katz and Tobolsky [9], or to stress support by hydrogen bonds that earlier had not been in stress-supporting positions. Further experimentation is necessary to fix the reason for this deviation.

Figure 2 is a log-log plot of the variation of the observed rate constant, k_o, with cysteine concentration at pH 6.5 for different temperatures. The rate constant is determined from the slope of a separate plot of the logarithm of relative force against time. The sets of points in Figure 2 are fitted with lines of slope unity, and these indicate that the rate constant is proportional to the first power of cysteine concentration at pH 6.5. It is concluded that the scission-controlling process is bimolecular, involving the reactions of only one cysteine molecule with the cystine cross-linkage, in accordance with the two-step scheme of reaction (1*a*) and (1*b*).

The reaction between the cystine disulfide bonds of keratin with cysteine solutions was studied as a function of pH. The results of these experiments are shown in Figure 3. It is evident that the rate of stress relaxation, and consequently the rate of the scission reaction, decreases considerably with decreasing pH. This result is in agreement with the studies of Bersin and Steudel [1] on cystine and thioglycolic acid. It is probably due, as suggested by these workers, to the effect of pH on the dissociation of the sulfhydryl groups of cysteine, and indicates that the group active in the scission reaction is the $CysS^-$ ion. This ionization precedes the reaction step, and the modified reaction mechanism is

$$CysSH \rightleftharpoons CysS^- + H^+ \tag{7}$$

$$RSSR + CysS^- \overset{k'_1}{\rightleftharpoons} RSS\text{—}Cys + RS^- \tag{8}$$

$$RSS\text{—}Cys + CysS^- \rightleftharpoons Cys\text{—}SS\text{—}Cys + RS^- \tag{9}$$

$$RS^- + H^+ \rightleftharpoons RSH. \tag{10}$$

If the ionization reaction (7) is much more rapid than the scission reaction (8), equation (6) describing the kinetics of the process as measured by stress relaxation in terms of disulfide bond scission becomes

$$\frac{f(t) - f(\infty)}{f(0)} = \left[1 - \frac{f(\infty)}{f(0)}\right] \exp(-k_1[CysS^-]_o t), \tag{11}$$

where $[CysS^-]_o$ is determined by the ionization constant, K, for reaction (7):

$$K = \frac{[H^+]_o[CysS^-]_o}{[CysSH]_o}. \tag{12}$$

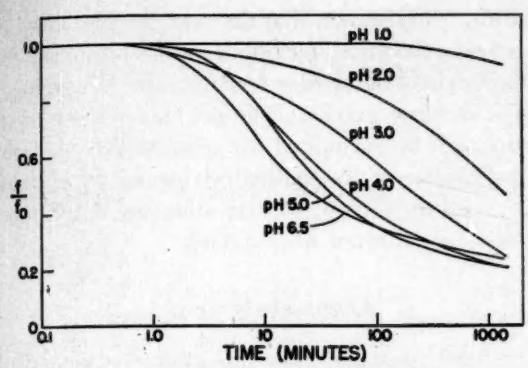

FIG. 3. *The stress relaxation of Columbia 56's wool fibers at 30°C and 15% extension for 0.049M cysteine at different pH values.*

From the temperature dependence of the reaction rate constant k'_1 it is possible to determine the heat and entropy of activation of the scission reaction (8), provided that the behavior of the ionization constant for reaction (7) is known over the range of temperature studied. This constant will not change much with temperature if the heat of ionization of the sulfhydryl groups is small, as has been suggested by several workers [2, 4, 13]. If this suggestion is accepted, the reaction rate constant, k'_1, is obtained from the plot of Figure 1 by dividing the observed rate constant, k_o, at a given cysteine concentration by that concentration, and then multiplying by $[H^+]/K$. The pH for the experiments of Figure 2 is 6.5 ± 0.15; and the pK for reaction (7) when R_o contains

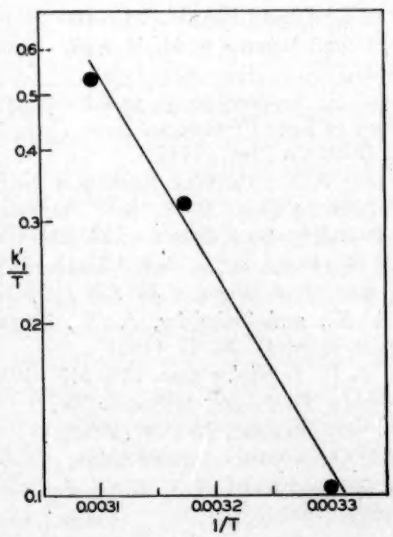

FIG. 4. *The plot of* k'_1 *divided by the absolute temperature on a logarithmic scale against the reciprocal of the absolute temperature.*

a $-NH_3^+$ group is given as 8.66 in the range 12°–37°C [3, 13]. The variation of rate constant, k'_1, with absolute temperature, T, determines $\Delta H^{\ddagger}$, the heat of activation, and $\Delta S^{\ddagger}$, the entropy of activation, through the following equation from the absolute theory of reaction rates [6]:

$$k'_1 = \frac{kT}{h} \exp\left\{ -\frac{\Delta H^{\ddagger}}{RT} + \frac{\Delta S^{\ddagger}}{R} \right\}, \qquad (13)$$

where k is Boltzmann's constant, h is Planck's constant, and R is the gas constant. The quantities $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are obtained from the slope and intercept, respectively, of a plot of $\ln (k'_1/T)$ against $1/T$, as shown in Figure 4. The heat of activation is found to be 18.2 kcal./mole, and the entropy of activation 8.8 entropy units.

The effect of pH on stress relaxation of single wool fibers in cysteine solution is shown in Figure 3, as mentioned earlier. Decrease in pH results in a strong decrease in reaction rate constant, as would be consistent with the mechanism (7) and (8) involving ionization of the sulfhydryl group; but the quantitative agreement demanded by equations (11) and (12) is not obtained. The rate constant is found to vary not as the first power of the hydrogen ion concentration, but rather more slowly. One explanation for this discrepancy lies in the possible variation of the ionization constant K with pH, owing to the presence of charged or uncharged amino and carboxylic groups in the cysteine molecule. Another explanation is that the rate constant for the scission of the cystine disulfide bond of keratin is sensitive to the presence or absence of charged groups within the molecule. Because of this unresolved difficulty in the pH dependence, the value of 8.8 entropy units obtained for the entropy of activation at pH 6.5 cannot be taken very seriously at this time. On the other hand, it is believed that the value of 18.2 kcal./mole obtained for the energy of activation is fairly reliable, for it should differ from the correct value only by the heat of ionization of the sulfhydryl group, which is thought to be small. The value of 18.2 kcal./mole obtained here for the cystine-cysteine reaction is close to the value of 11–15 kcal./mole for the cystine-thioglycolic acid reaction measured by Bersin and Steudel [1]; but since they were studying the complete reduction (8) and (9), rather than just the first step (8), there is a slight chance that the agreement may be only fortuitous.

If the cystine content of the fiber is known, then the number of cross-links ruptured can be calculated

as a function of time from the integrated form of equation (3) under the assumption that all cystine disulfide cross-links contribute equally to the support of stress. In case only a fraction of the disulfide bonds in a sample contribute to the support of stress on a given extension of the sample, the calculated number of cystine bonds broken as a function of time will only be an upper limit. But several difficulties are involved in carrying out this calculation. Because of fiber-to-fiber variation of the cystine content [12], it is desirable that the cystine content of the individual fibers be known. However, the conventional analytical technique requires the hydrolysis of the sample, and, consequently, the analysis cannot be made in advance of the stress-relaxation experiments. Determination of the cystine content after the relaxation experiments is difficult by conventional techniques when cysteine is the reagent, because any of this substance retained by the fiber by adsorption will interfere in the analysis. As a consequence, the average cystine content must be used. This procedure will, of course, introduce an amount of uncertainty, dependent on the fiber-to-fiber variation. For the fibers used in these experiments, the cystine content was found to be 10.6% on a dry-weight basis,* with the standard deviation from fiber to fiber estimated to be perhaps 2%. Then, knowing the volume of the fiber and its density, it is possible to obtain an equation for the rate of scission of the disulfide bonds in the fiber. It must be kept in mind, however, that the direct application of the data presented here to other keratin fibers may not be valid, since it is quite possible that the rate of stress relaxation of a keratin fiber will be dependent to a certain extent upon fiber type. Indeed, experiments are now in progress in this laboratory to determine the rate of stress relaxation of different types of keratins in the presence of various reducing agents.

Summary

A discussion of the kinetics of the reaction between cysteine in solution and cystine in keratin is presented. The reaction was followed by means of the stress-relaxation technique as a function of cysteine concentration, hydrogen ion concentration, and temperature. It is shown that the reaction measured by the stress-relaxation technique is bimolecular, following pseudo first-order kinetics when cysteine is present in large excess. The pH dependence of the reaction can be accounted for qualitatively in terms of dissociation of the sulfhydryl groups of cysteine. A heat and an entropy of activation are determined, and their significance is discussed.

* The analysis of the Columbia 56's wool fibers was carried out by Mr. E. B. Jeffries of the Textile Research Institute laboratories by a micro-method based on the work of Folin [5].

Acknowledgment

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The α-β Transformation in Stretched Hair

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Abstract

The interpretation of the x-ray diffraction diagram of hair, both natural and stretched, is considered, and attention is drawn to the importance of considering the amorphous as well as the crystalline parts of hair.

Infrared spectra show that there is a mixture of α and β structures (folded and extended polypeptide chains, respectively) both in natural hair and in hair which has been extended 100%, and that the orientation of the β material, at least, is very imperfect. It is concluded that in such a system no simple relationship exists between the extension of the molecular chains on unfolding and the extension of the whole fiber.

Introduction

The experiments of Astbury and Street [4] and Astbury and Woods [5] on the x-ray diffraction patterns given by natural and by stretched wool and hair have been the starting point for much experimental work and a good deal of speculation concerning the physical structure of proteins. As is well known, Astbury and coworkers found a diffraction pattern (the α pattern) in natural wool and hair which disappeared on stretching, to be replaced by a different pattern (β). From considerations based on the magnitude of the observed lattice plane spacings, these forms were ascribed, respectively, to a folded and an extended configuration of polypeptide chains.

It was also observed that wool or hair stretched in water, steam, or 1% caustic soda solution was capable of an extension of about 100% before rupture. The stretched material could be relaxed in the medium in which the stretching was carried out, and in the case of stretching in alkali, it was claimed that the extension was reversible. Stretching in water or steam, on the other hand, produced an extension which was not reversible, the load-extension curve not being reproduced during successive cycles.

These experiments have been interpreted by Astbury and coworkers as showing decisively that the α-β transformation which occurs on stretching is accompanied by a molecular extension of 100%, and Astbury has maintained this interpretation in many subsequent papers. The validity of such an interpretation is obviously a matter of great importance, and it has been the subject of much controversy, usually in connection with various models for the α folded polypeptide chain which have been advanced from time to time. It is evident that if natural hair consisted entirely of well-oriented α chains, and if after a (reversible) stretch in alkali solution only well-oriented β chains were present, no alternative to the above interpretation could be put forward. Examination of the published x-ray diffraction photographs of natural wool and "generalized wool"—*i.e.*, wool which has been extended 100% in 1% NaOH solution and then allowed to relax—suggests, however, that this may by no means be the case. There is, in addition to the sharp arcs which originate from crystalline regions in the wool, a very strong diffuse ring which appears to indicate a large amount of unoriented amorphous material. This ring is particularly strong, relative to the sharp arcs, in generalized wool. Undoubtedly, in the photograph of generalized wool (Astbury and Woods [5]) the total intensity in the ring is several times as great as in the arcs.

These facts, which (along with many more) are to be found in the original papers of Astbury, Street, and Wood, might suggest that caution should be used in relating the bulk extension to the extension of the molecules in the α-β transition. Nevertheless, some recent authors (Rudall [14]; Bragg, Kendrew, and Perutz [6]; and Pauling and Corey [13]) appear to accept this conclusion. Others, on the other hand, have rejected it (Elöd and Zahn [10]; Bull and Gutman [7]; and Ambrose and Elliott [1]). In this unsatisfactory state of affairs, it seems essential to have more experimental evidence bearing on the question. The use of polarized infrared radi-

ation, which has already produced useful new information on protein and polypeptide structure, seemed to be a promising method, and the following sections describe some results obtained at this laboratory.

Experimental

For several reasons, the observations described herein were made in the overtone region. This enables fairly thick specimens (about 0.3 mm. thick) to be employed, which allows x-ray observations to be made on the same sample used for infrared spectroscopy. In addition, it is extremely difficult to cut the very thin longitudinal sections from a thin hair (*e.g.*, human hair) if observations are to be made in the fundamental region, whereas a suitable specimen for the overtone region can be made readily by making up a bundle of fibers. In all cases, the fibers were mounted in small glass cells containing a mixture of carbon tetrachloride and carbon tetrabromide, a liquid which matches the refractive index of hair sufficiently well to reduce surface reflection to a small amount.

The technique was essentially the same as that employed in connection with haemoglobin (Elliott and Ambrose [9]) and ribonuclease crystals (Elliott [8]), making use of a low-power reflecting microscope. For stretching hair, individual hairs were held under tension by a suitable weight and were then subjected to the action of steam or 1% caustic soda solution. Two records of each specimen were made in each of the two polarizer positions employed, to check for possible movement of the specimen or its cell in the oscillating mechanism employed to give records in the "cell in" and "cell out" positions. The spectra shown in Figures 1, 2, and 3 were drawn from pairs of records which were in very good agreement.

Although these figures represent accurately the spectrum of a particular specimen, mounted in a particular position, it must be realized that changes occur if another part of a multifiber specimen is used. The change is probably due to small changes in reflection losses at the surfaces of the fibers. The reflection losses, in general, are different for different positions of the polarizer, and, because of this, small adjustments in the relative positions of the "parallel" and "perpendicular" spectra were made so that they would have equal densities in the transparent region beyond 5300 cm.$^{-1}$. As optical densities are used throughout, this procedure introduces no distortion of the spectra.

An x-ray diffraction spectrum was made for each hair specimen. These spectra are not reproduced, since, with two exceptions (see next section), they appeared to be similar to those published by Astbury and coworkers.

In general, it was found that the hairs were capable of very roughly 100% extension—that is, some specimens survived this extension whereas others did not. A time-extension curve was drawn for a horsehair specimen (subsequently used for the infrared record of Figure 2). The extension (under constant load in steam) was stopped at 86% elongation. At this point the curve was rising slowly and it did not appear that it would reach 100%. The other stretched specimens of hair were extended 100%.

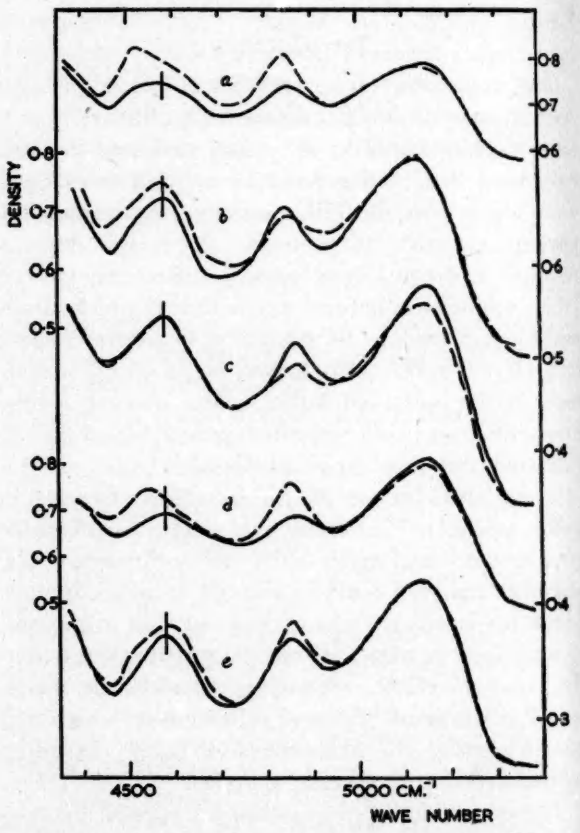

FIG. 1. a—*Human hair stretched 100% in steam.* b—*Natural human hair.* c—*Human hair stretched 100% in 1% NaOH, relaxed, washed, and dried.* d—*Human hair stretched 100% in 1% NaOH, and washed and dried under tension.* e—*Human hair stretched 90% in 1% NaOH, relaxed, washed, and dried (second specimen).* Solid line—E *vector perpendicular to fiber axis.* Broken line—E *vector parallel to fiber axis. The position of the* $C=O$ *combination peak for the "perpendicular" spectrum of natural hair is indicated on each spectrum.*

Results and Discussion

The lithium fluoride spectrometer used in the work described here was recalibrated, using ethylene dibromide ($CH_2Br \cdot CH_2Br$) and ethylidene dichloride (CH_3CHCl_2), whose absorption bands had been measured by Spence and Easley [15] on a grating instrument. This recalibration showed that earlier results for the N—H combination band in fibrous proteins (Ambrose and Elliott [2]) and in some crystalline proteins (Elliott and Ambrose [9] and Ambrose and Elliott [3]) are about 20 cm.$^{-1}$ too low. The values for the C=O combination band appear to be about 10 cm.$^{-1}$ too high. This revision does not in any way affect the conclusions drawn in earlier papers, which depended upon the dichroic effects observed.

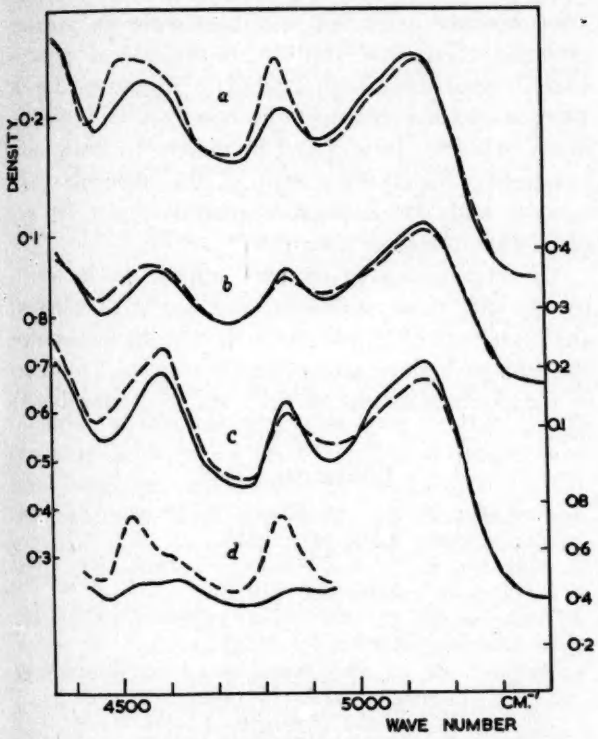

FIG. 2. a—*Horsehair stretched 86% in steam.* b—*Natural horsehair.* c—*Porcupine quill.* d—*Silk suture.* Full line—E *vector perpendicular to fiber axis.* Broken line—E *vector parallel to fiber axis.*

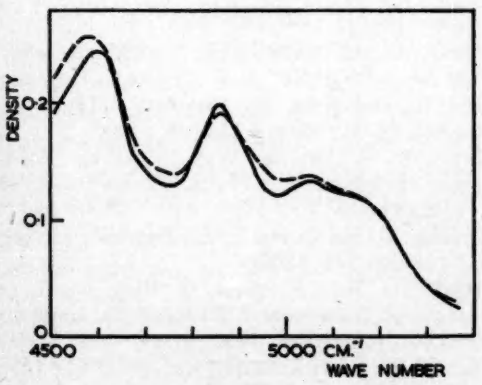

FIG. 3. *Horsehair dried* in vacuo.

The spectra reproduced in Figures 1, 2, and 3 show, in agreement with earlier results [2], that the N—H combination band at approximately 4860 cm.$^{-1}$ has perpendicular and parallel dichroism in α and β structures, respectively. For this band, there is little or no appreciable difference in frequency between bands in α and in β polypeptides. The band at approximately 4590 cm.$^{-1}$, on the other hand, does show a small, but quite appreciable, frequency shift towards lower frequency when a protein or polypeptide is changed from the folded (α) to the extended (β) configuration. In poly-γ-methyl-*L*-glutamate this shift is about 75 cm.$^{-1}$. Evidence based on observations in compounds of known structure suggests strongly that it is a C=O combination mode. In a well-oriented β structure such as silk suture, as shown in Figure 2, it shows very high parallel dichroism, and is in this respect similar to the N—H combination band. The band at 5150 cm.$^{-1}$ is caused largely by water in the protein, but the small shoulder at about 5060 cm.$^{-1}$ which can be seen on some spectra may be due to amide groups [8]. Figure 3 shows the spectrum of horsehair dried *in vacuo,* with the intensity of this band greatly reduced. In this specimen the band at 5060 cm.$^{-1}$ shows clearly, and appears to be dichroic. There is little doubt that the spectrum of well-dried proteins in this region would prove interesting.

If we examine the spectra of hair with the foregoing facts and deductions in mind, we note at once that hair which has been extended 100% in alkali or in steam, although showing dichroism of the same character as silk, is very much less dichroic. This must mean that the β chains are very imperfectly oriented, or that there is a considerable fraction of α material which has survived the extension, or that both of these conditions occur. In a perfectly oriented extended β polypeptide, we should expect disappearance of the C=O and N—H bands for the "perpendicular" positions of the polarizer, and silk suture approximates this condition fairly well. The asymmetric character of the C=O band in stretched hair shows very clearly the presence of two bands, without doubt the (unresolved) C=O modes of the α and β configurations. As Astbury and coworkers have shown, the crystalline α diagram cannot be de-

tected in hair which has been extended 100%; it follows, therefore, that the α material revealed by the infrared spectra must be amorphous. As a matter of fact, the α diagram, although not present in x-ray diagrams of the hair specimens used for the spectra of Figures 1 and 2, can be detected in elephant hair which has been extended 100% in steam.

In unstretched natural hair the low dichroism of the spectra shown is not, in itself, evidence of poor orientation, since the dichroism to be expected in a perfectly oriented α fibrous protein is not known. In a moderately oriented α polypeptide the N—H band has been found to have a dichroic ratio of about 3 : 1, whereas the C=O band has a ratio near unity. Hair shows much the same dichroism as porcupine quill, in which the crystallites at least are well oriented (MacArthur [11]). Again, however, the asymmetry of the C=O band shows a two-component structure, the considerably higher "parallel" dichroism on the low-frequency side showing the presence of β protein. This has also been shown for elephant hair and porcupine quill in the fundamental region [2]. Since the characteristic β arcs do not appear on the x-ray diagram of natural hair, it must be concluded that the β component (which is by no means negligible in amount) is amorphous.

Features similar to those of natural and steam-stretched hair are shown by generalized hair and hair which has been dried under tension after stretching in 1% caustic soda solution. We again have evidence of an α component in the stretched (predominantly β) material, and of a β component in the relaxed generalized hair.

Results for generalized hair have been found to vary markedly from one specimen to another, and Figure 1 shows the spectra of two samples which have been stretched approximately 100% and then relaxed in 1% caustic soda solution. One specimen shows the dichroism and x-ray pattern of an α fiber, but the dichroism in the spectrum shown at the bottom of the figure suggests a poorly oriented β fiber. This specimen did not show a distinct α spacing on the x-ray diffraction photograph, but was almost completely amorphous. In spectra of the overtone region, absorption bands usually appear superposed on an apparently dichroic background, which may result from "form dichroism" caused by the fibrous nature of the specimen and from reflection effects. At the same time, there may be a genuinely dichroic absorption region of considerable width. For these reasons, the dichroism of a band must be judged from its density after subtraction of the background density in the neighborhood. Uncertainty in determining this background density imposes a serious limit on the accuracy which can be obtained. Nevertheless, the semiquantitative results so obtained are of considerable value.

It is now evident that the picture drawn from observations of the diffraction arcs in the x-ray patterns given by wool and hair is quite misleading, since it entirely leaves out of account the existence of amorphous material, containing both α and β chains, which is of low orientation even in the stretched material. This amorphous fraction is almost certainly greater than the "crystalline" fraction; in the case of "generalized" wool, on which Astbury's argument for a 100% molecular extension is based, it is probably much greater. It is quite impossible to draw any conclusions about the extent of the molecular extension, and this important quantity must be regarded at present as unknown.

The conclusions given here appear to be compatible with those of Meyer, van der Wyk, Gonon, and Haselbach [12], who consider that the long-range elasticity of keratin arises from the thermal motions of the chain segments in the swollen (amorphous) fiber.

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Studies on the Partial Carboxymethylation of Cotton

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Abstract

Additional studies have been made on partial carboxymethylation—the reaction between monochloroacetic acid and cotton in the presence of sodium hydroxide—and on the products obtained. A thorough investigation of the time and temperature of reaction and concentration of reagents showed that relatively small amounts of monochloroacetic acid, properly applied, alter the properties of cotton considerably.

Pilot-scale carboxymethylation of cloth was conducted which showed that it is possible to use standard textile machinery in the process. The cloth resulting from this treatment had a crisp hand with a slightly starched feel.

More detailed investigations than reported previously were made, and it was found that the tensile strength and elongation of treated cotton are increased, dyeing properties are changed, and soiling-resistance and soil removal are increased. It was also learned that the treated materials are unaffected after one year's storage.

THE PARTIAL CARBOXYMETHYLATION of cotton at this laboratory has been reported in two previous publications [8, 9], and two patents have been issued on uses for the modified cotton [2, 10]. This paper reports additional data that have been obtained on the reaction and on the properties of the products.

Carboxymethylation produces significant changes in the physical and chemical properties of cotton, depending upon the degree of substitution. For example, a relatively strong treatment, to effect a substitution of one carboxymethyl group per one to three anhydroglucose units, will result in a product which is soluble in water. The authors have successfully treated cotton to this state while retaining its fibrous character and much of its original tensile strength [11]. Cotton that is treated to obtain a substitution of about one carboxymethyl group per 7 to 50 anhydroglucose units will have changed physical and chemical properties, and will be insoluble in water but highly swellable. It is this range of substitution with which this paper is concerned. The new properties of modified cotton in this range of substitution may be utilized to advantage for other treatments—for example, in the production of crease-resistant cloth, a use which is described elsewhere [3].

For a textile process to be commercially feasible, it must not increase the cost of cotton cloth excessively. Consequently, an investigation was undertaken to ascertain the most efficient and the most economical conditions for the partial carboxymethylation of cotton. This necessitated a study of the carboxymethylation reaction itself, a study of the possibility of using ordinary textile machinery in the process, and a study of effects of the treatment on the important textile properties.

Study of Reaction Conditions

Effect of Reagent Concentration

The carboxymethylation process consists simply of impregnating cotton with a solution of monochloroacetic acid followed by treatment with a strong solution of sodium hydroxide. Cotton, in the form of a 12/5 sewing thread, was extracted with acetone to remove waxes, soaked in aqueous monochloroacetic acid solution for 3 min., centrifuged to about 60% pickup, and then placed in excess sodium hydroxide solution for 30 min.

Five percentages of monochloroacetic acid, from 5% to 25%, were each used with 30%, 40%, and 50% sodium hydroxide. The treated samples were

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washed with distilled water and analyzed by back-titration of acid groups to determine the degree of substitution. It was found, as seen from the data in Table I, that as the concentration of the sodium hydroxide is increased, higher degrees of substitution are obtained with less monochloroacetic acid.

These results indicated that the concentration of the costlier reagent, monochloroacetic acid, could be lowered, and effective substitution obtained by raising the concentration of the less expensive alkali. Accordingly, 50% sodium hydroxide was used on cloth padded with 2%, 4%, 6%, and 8% monochloroacetic acid solutions. These treatments resulted in substitution ratios of 0.024, 0.032, 0.037, and 0.048 (1:42, 1:31, 1:27, and 1:21 carboxymethyl group per anhydroglucose units), respectively.

Effect of Temperature

In the laboratory studies described above, the reactions were carried out at room temperature. To get complete and uniform reactions, periods of time of 20–45 min. were required. During this time the reaction between the monochloroacetic acid and the sodium hydroxide caused the temperature to rise to 40°–50°C. Obviously, the relatively long period of treatment of cloth with sodium hydroxide solution would make the process impractical for commercial production. Accordingly, a laboratory study was made to determine whether the reaction could be expedited by a temperature elevation.

Pieces of cloth were padded with a solution of 15% monochloroacetic acid and immersed in excess 40% sodium hydroxide solution at temperatures ranging from 27° (room temperature) to 87°C for exactly 45 sec. After this time the reaction was halted by plunging the sample into cold running water, which effectively removed the reactants and washed the samples. Results, shown in Table II, reveal that the highest substitutions were obtained by using sodium hydroxide heated to 67°–77°C.

A similar set of samples was run at subnormal temperatures as low as 5°C, and it was found that very little, if any, reaction takes place in the cold.

TABLE I. EFFECT OF REAGENT CONCENTRATION ON DEGREE OF CARBOXYMETHYLATION

Monochloroacetic acid (%)	Carboxymethyl substitution* 30% NaOH	40% NaOH	50% NaOH
5	1:49 (0.020)	1:28 (0.036)	1:27 (0.037)
10	1:28 (0.036)	1:14 (0.071)	1:14 (0.071)
15	1:23 (0.043)	1:13 (0.077)	1:11 (0.091)
20	1:19 (0.053)	1:9 (0.111)	1:8 (0.125)
25	1:15 (0.067)	1:8 (0.125)	1:7 (0.143)

* Substitution is expressed as one carboxymethyl group per *n* anhydroglucose units. Values in parentheses are the degrees of substitution, with the ratio of carboxymethyl groups to anhydroglucose units expressed as a decimal fraction.

Pilot-Plant Scale Carboxymethylation

To determine the feasibility of using standard textile machinery in the carboxymethylation process, a pilot-plant scale treatment of 100 yds. of 80-square cotton print cloth was made. The cloth was padded on a 50-in., 2-roll padder with one dip through 17.6% aqueous monochloroacetic acid containing 0.5% of a wetting agent. The cloth was collected on a roll and weighed for wet pickup, which was 73.3%. It was then run through a 42% sodium hydroxide solution and padded with just sufficient pressure to remove the excess alkali and increase the pickup to about 105% on the weight of the cloth. The cloth was collected on a roll and allowed to stand for 45 min. The temperature inside the roll did not exceed 50°C. The cloth was washed on a jig five times with water at room temperature, and then five times with water at 82°C. Carboxymethyl substitution was 0.065, or about one carboxymethyl group per 15 anhydroglucose units, and did not vary appreciably in different sections of the roll. After washing, the cloth was passed over steam-heated drying cans. Another portion of cloth was treated for control purposes by padding with water containing a wetting agent and then mercerized without tension with a 42% soduim hydroxide solution.

TABLE II. EFFECT OF TEMPERATURE ON DEGREE OF SUBSTITUTION*

Temperature of reaction (°C)	Carboxymethyl substitution†
27 (room temperature)	1:85 (0.012)
37	1:55 (0.018)
47	1:35 (0.029)
57	1:18 (0.056)
67	1:14 (0.071)
77	1:9 (0.111)
87	1:18 (0.056)

* Samples were treated with 15% monochloroacetic acid and 40% sodium hydroxide for 45 sec.

† Degree of substitution is expressed as one carboxymethyl group per *n* anhydroglucose units. Values in parentheses are the degrees of substitution, with the ratio of carboxymethyl groups to anhydroglucose units expressed as a decimal fraction.

This treatment would indicate that, as far as equipment is concerned, the process is commercially feasible using existing textile machinery. In a private communication [13], it was learned that plant-scale carboxymethylation has been carried out successfully in 45 sec. on a slightly modified mercerizer unit in continuous process.

Properties of Carboxymethylated Cotton Textiles

The increased water absorbency of carboxymethylated cotton has been reported in earlier work [9]. Other important changes in the fiber, yarn, and fabric properties of cotton which has been carboxymethlated have now been noted.

Physical Properties

Chemical modifications of cotton usually result in some strength loss. To determine whether this was true of carboxymethylation, a set of 7/2 mercerized cotton thread samples was treated with 5% to 30% monochloroacetic acid solution and 50% sodium hydroxide. Skeins of the thread were soaked in the respective acid solution, then centrifuged to 60% pickup, and soaked in an excess of sodium hydroxide solution (just enough to cover the thread) for 30 min. to effect a substitution of from 0.015 to 0.100. The usual rise in temperature due to acid-base neutralization was noted. The skeins were neutralized with alcoholic acetic acid, washed in alcohol, and dried under slight tension to restore approximately the original skein length.

Tests on the samples showed that both breaking strength and elongation at break are actually increased by modification (see Table III). Gage increases slightly, while count or yarn number decreases. This decrease was probably due to an increase in linear density arising from an increase in weight, in moisture regain, and some shrinkage. The slight increase in weight due to the addition of carboxymethyl groups is shown graphically in Figure 1.

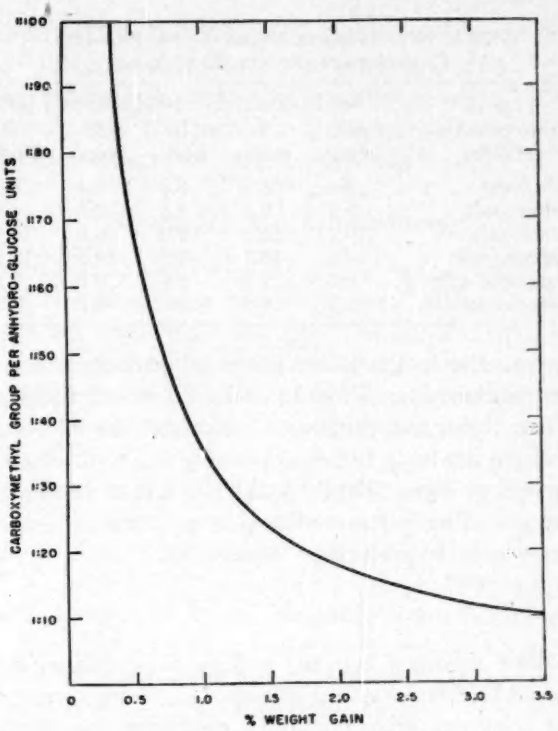

FIG. 1. *Calculated weight gain effected by partial carboxymethylation of cotton.*

The breaking strength increases shown in Table III

TABLE III. EFFECT OF CARBOXYMETHYLATION ON PHYSICAL PROPERTIES OF COTTON THREAD

Treatment: Monochloroacetic acid solution (%)	Treatment: Sodium hydroxide solution (%)	Carboxymethyl substitution*	Breaking strength (lbs.)	Elongation (%)	Gage (in.)	Yarn number (cotton system)
0†	0	0	8.5	5.7	0.0170	3.37
5	50	1:65 (0.015)	9.3	9.9	0.0208	2.85
10	50	1:20 (0.050)	9.7	10.1	0.0208	2.86
15	50	1:16 (0.063)	9.1	10.5	0.0202	2.96
20	50	1:13 (0.077)	9.6	9.6	0.0204	2.94
25	50	1:11 (0.091)	10.2	11.4	0.0205	2.96
30	50	1:10 (0.100)	10.0	10.4	0.0208	2.92

* Carboxymethyl substitution is expressed as one carboxymethyl group per n anhydroglucose units. Values in parentheses are the degrees of substitution, with the ratio of carboxymethyl groups to anhydroglucose units expressed as a decimal fraction.

† Untreated control.

TABLE IV. STORAGE STABILITY OF PARTIALLY CARBOXYMETHYLATED CELLULOSE

Type of carboxymethyl-cellulose	Breaking strength (single strand) (lbs.) 0 weeks	8 weeks	16 weeks	32 weeks	52 weeks
Acid form	8.4	8.5	8.8	9.4	8.2
Sodium salt	9.5	9.3	9.5	9.5	9.8
Cupric salt	10.2	10.2	9.9	10.6	10.4
Mercuric salt	10.3	10.5	10.8	10.3	10.3
Aluminum salt	9.6	9.6	9.7	9.8	9.5
Ammonium salt	8.2	9.1	8.6	8.7	8.5

are peculiar to the lower ranges of partial carboxymethylation, from 0.010 to about 0.150 substitution. When higher substitutions are obtained, the breaking strength begins to decrease, possibly due to the washing off of some slightly soluble material produced near the fiber surface or to a heavy localized reaction which tends to cause weak spots.

Stability During Storage

Some modified cottons, notably oxycellulose, are known to deteriorate on storage [4], losing strength and becoming discolored. To determine the effects of storage on partially carboxymethylated cotton in several forms, six skeins of 12/5 cotton sewing thread were treated with 20% monochloroacetic acid solution and 50% sodium hydroxide to effect a substitution of 0.077, or one carboxymethyl group per 13 anhydroglucose units. The thread skeins were converted to the free acid from the sodium form by soaking in 2% aqueous hydrochloric acid for 1 hr., after which they were washed with distilled water. One skein was left in the acid form; the others were converted to various salts by soaking in aqueous solutions containing the appropriate cations. The results shown in Table IV indicate that there is no loss of strength of carboxymethylated cotton during storage for 1 year.

Dyeing Characteristics

Brief mention is made in another paper of the resistance of partially carboxymethlated cotton to direct cotton dyes [3]. A rather extensive study of the dyeing of the carboxymethylated 80-square cloth with 0.065 substitution was carried out as follows: Five classes of dyes—substantive, vat, basic, azoic, and sulfur—were used in 2% dyeings. A control cloth, mercerized without tension, was dyed simultaneously with the carboxymethylated cloth in the form of the sodium salt to detect differences, if any, in color, washfastness, and lightfastness. Samples were washed according to Test Method No. 2 in "Colorfastness to Commercial Laundering and to Domestic Washing," American Association of Textile Chemists and Colorists [1]. Samples were exposed in the Fade-Ometer * in order to determine lightfastness.

Substantive dyes used were National Solantine Blue 4GL (Prototype No. 26), Chlorantine Fast Blue 4GL (Color Index No. 533), and Triazol Fast Red B (Color Index No. 382). The carboxymethylated cloth did not dye as well as the mercerized cloth for it resisted the dye until sodium sulfate was added to the dye bath.

Two vat dyes, Ponsol Blue GDD (Color Index No. 1112) and Ponsol Jade Green D (Color Index No. 1101) did not dye the carboxymethylated cloth uniformly and did not penetrate the constituent yarns.

A basic dye, Methylene Blue 2B (Color Index No. 992) had a greater affinity for the carboxymethylated cloth than for the mercerized cloth in the samples that had the tannin mordant as well as in the samples which were not mordanted, but the modified samples did not withstand the standard wash. This is explained by the fact that the dye is known to react with the carboxyl group [6] and is replaceable by a stronger cation, such as sodium, found in the wash solution.

The azoic dyes, Naphthol AS-SW-Fast Red Salt 3GL and Naphthol AS-SW-Fast Blue Salt BBN, had a greater affinity for the carboxymethylated cloth than for the mercerized cloth. The standard wash test did not affect the color of these samples. The carboxymethylated cloth samples withstood the Fade-Ometer tests better than the mercerized cloth.

Sulfur dyes, Sulfogene Brilliant Green 4GX (Color Index No. 1006) and Sulfogene Cutch MCF, did not dye the carboxymethylated cloth uniformly and did not penetrate the yarns.

In these tests, except in the cases noted, the washfastness and lightfastness of dyed carboxymethylated cloth were the same as for the mercerized cloth.

It has been found that when plain cloth is first dyed and then carboxymethylated, the problem of dye-resistance is overcome. The dye, of course, must be fast to caustic solutions.

* The mention of trade products in this paper does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

Soiling-Resistance and Soil Removal

The improvement in soiling-resistance of fabrics by treatment with a solution of sodium cabroxymethylcellulose has been described by Muhr [7] and by Strickland [12]. Utermohlen and coworkers [14, 15], under a contract supervised by this laboratory, made a study of various modified cottons, such as mercerized, partially acetylated, partially aminoethylated, and partially carboxymethylated cottons. They found that mercerization and partial carboxymethylation definitely increase resistance to soiling from aqueous soil dispersions, and that partial carboxymethylation produces fabric having the greatest ease of soil removal. A possible explanation for this phenomenon offered by Utermohlen is that the most promising treatments all have the ability to confer cation-exchange properties to the cloth.

Cation-Exchange Properties

The acid groups introduced during the etherification of cotton with monochloroacetic acid will exchange cations in proportion to the degree of substitution. This property of the treated cloth has been discussed by Hoffpauir and Guthrie [5] in connection with other modified cottons. The acidity of the carboxymethylated cotton (pH 3.65) has been found to be sufficient to catalyze the condensation of crease-proofing resins such as methylolmelamine and methylolurea. A patent has been issued on the process [2], and the process and the properties of the products have been described elsewhere [3].

Wearability of Partially Carboxymethylated Cotton Cloth

The cloth produced in the pilot-scale run had a crisp hand with a slightly starched feel, indicating possible use as a permanently starched fabric for scarves, shirts, blouses, and other textile products where a starched effect is desirable.

To test the wearing qualities of such material in actual use, two women's blouses of the same design were made of modified and of mercerized control cloth. The seamstress who made the blouses reported that the carboxymethylated cloth was much superior in sewing qualities to the mercerized cloth because of its full hand. These blouses were worn for the same periods of time in active sports use by a laboratory employee, and were washed and ironed the same number of times over a period of 18 months. At first, the carboxymethylated blouse felt slippery when placed into the wash water; however, this feel disappeared after a few washings. The carboxymethylated blouse was described as being easier to iron than the mercerized blouse, and its semi-starched appearance made it more attractive.

Summary and Conclusions

Additional studies on the partial carboxymethylation of cotton have revealed several factors which have not been previously described in detail:

(1) Concentrations of monochloroacetic acid as low as 4%–8% are sufficient to obtain carboxymethyl substitutions from 0.032 to 0.048 provided strong alkali is used.

(2) Increased reaction from the same concentration of reagents may be obtained by increasing the temperature of the sodium hydroxide to about 67°–77°C. Negligible reaction occurs below 10°C; above 80°C substitution is not increased.

(3) Partial carboxymethylation in the range of 0.010 to 0.150 substitution increases the breaking strength and elongation of cotton thread.

(4) Carboxymethylated cotton in several forms does not deteriorate during storage.

(5) Carboxymethylated cotton may be dyed as well or better than mercerized cloth with azoic dyes; it does not dye as well with substantive, vat, or sulfur dyes. It has a great affinity for basic dyes, but these dyes are not washfast. However, untreated cloth which has been dyed previously may be carboxymethylated without affecting the color, provided the dye used is stable to alkaline solutions. Lightfastness of azoic-dyed carboxymethylated cloth is better than that of mercerized cloth.

(6) Partially carboxymethylated cloth will resist soiling and facilitate soil removal to a noticeable extent.

(7) The acidic carboxymethyl group will exchange cations with salts, and is strong enough to catalyze the condensation of amino resins to produce crease-resistance.

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Crease-Resistant Cloth from Partially Carboxymethylated Cotton

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Abstract

A method of applying resin treatments to the acid form of partially carboxymethylated cotton cloth to produce crease-resistance has been developed. The acidity of the carboxyl group and the higher swellability are advantageous for overcoming two difficulties met in the usual methods of producing crease-resistant cotton cloth by resin treatment. The presence of the acid carboxyl group supplies a built-in catalyst, making the addition of catalyst unnecessary, in this way avoiding the prepolymerization of resin baths which contain added catalysts. The high swellability of the modified cotton allows easier penetration of the resin-formers and larger pickup of resin, with the production of cloth of equivalent crease-resistance, of superior hand and abrasion-resistance, and better in most other physical properties, in comparison with the unmodified resin-treated cloth.

The process of carboxymethylation, which consists of impregnating cotton cloth with a weak solution of monochloroacetic acid followed by treatment with strong sodium hydroxide, is commercially feasible and can be carried out on ordinary textile equipment.

THE PREPARATION and properties of partially carboxymethylated cotton have been reported by this laboratory in several articles and in a patent [7, 16, 17, 18]. The process consists simply of impregnating cotton cloth with a solution of monochloroacetic acid followed by treatment with a strong solution of sodium hydroxide. The resulting cloth is the sodium salt of carboxymethylcellulose, which is easily converted to the acid form by soaking in dilute aqueous hydrochloric or sulfuric acid. The acidified, modified cloth has several properties, not possesed by ordinary cotton, that should make it of value to the textile industry. Two such properties are high swellability and acidity of the carboxyl group.

Since these two properties have certain theoretical advantages for the production of crease-resistant

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cotton, partially carboxymethylated cotton was given the usual creaseproofing treatments and the effects were studied. A method was developed, and is reported here, whereby carboxymethylated cotton is treated with resins to produce crease-resistant cloth which is superior in hand, abrasion-resistance, and most other physical properties to unmodified cotton cloth which received the same resin treatments. A public service patent [6] has been issued on this use of carboxymethylated cotton to obtain superior crease-resistance.

That the process of partial carboxymethylation is commercially feasible has been indicated by the facts that a small amount of monochloroacetic acid is sufficient to obtain the reaction to an effective degree, and that the process can be carried out easily on ordinary textile equipment [7].

The most complete summary of work on the theory, treatment, testing, and prospects of crease-resistant cotton has been published by Buck and McCord [3]. The literature from 1937 to 1949 on crease-resistant textiles has been surveyed by Horigan and Sage [13]. Nickerson [14] has studied the application of melamine-formaldehyde-type resins to cotton. Nuessle has reported the effect of the change of a number of variables in creaseproofing [15]. Gagliardi and coworkers [9, 10, 11] have reported on the physical properties of creaseproofed fibers and fabrics.

The first successful treatment of cotton for crease-resistance was developed in England in 1928 by Foulds and Marsh [8], who used alkali to swell the cloth, followed by washing and then impregnating the wet, swollen cloth with a resin-forming material. All the usual methods of imparting crease-resistance to cotton are based on the use of acids or acid-forming catalysts to polymerize the resin-former *in situ* in cloth.

Previously, such methods have been more successful on rayon than on cotton. This is due to rayon's greater swellability, arising from a lower crystalline-amorphous ratio, which allows more thorough penetration by the resin-formers [4]. It is known that the crystalline regions of unmodified cotton cellulose are not penetrated by creaseproofing resin-formers. Rather, the resin is deposited on the surfaces in these regions, and the result is a harsh finish [19]. The high swellability of the partially carboxymethylated cotton, due to the introduction of the strongly polar carboxymethyl group, or to its lowered crystalline-amorphous ratio [5], or both, should afford easy penetration of the resin-forming monomers and result in better resin deposition.

In ordinary creaseproofing treatments, curing takes place in the pH range of 4.5 [2] to 5.8 [14]. Lower pH's are desirable, but are not practicable because of resultant acid degradation of the cloth. Partially carboxymethylated cotton at half-capacity has a pH of 3.65 [12]. This lower pH should result in more effective catalysis in the condensation of the resin. Since the catalyst is built in, the liability to acid degradation is minimized.

Another difficulty in the usual treatments, which the acidity of the carboxyl group should overcome, is that the creaseproofing resins in the bath polymerize slowly on standing after the catalyst has been added. This sometimes results in the formation of resin molecules which are too large to penetrate the cellulose wall of the cotton fibers, and which therefore polymerize on the fiber surfaces. The result is a harsh, stiff hand in the treated cloth, with low tear strength and low abrasion-resistance. With the catalyst present as part of the modified cellulose molecule, the solutions are stable for a longer time, and the possibility of polymerization of the resin prior to impregnation is minimized. In the usual treatments, frequently whole batches of commercial cloth have little to no crease-resistance or have a harsh finish because of this prepolymerization of the resin bath.

Materials and Test Methods

Samples of 80-square cotton print cloth with carboxymethyl substitutions ranging from 0.024 to 0.067 were used. Degree of substitution is expressed as the ratio of carboxymethyl groups to anhydroglucose units. Detailed methods whereby substitution in this range can be obtained on pilot-plant equipment have been described in another paper [7].

The resins used were dimethylolurea (urea formaldehyde), as prepared by Tripp [20], and Resloom HP * (melamine formaldehyde). The cloth was impregnated by padding with an aqueous solution of the resin, then dried on a pin frame in a circulating-air oven, and cured. The commercial catalysts, tested for comparison, were diammonium phosphate and Monsanto Catalyst AC.

The Monsanto Crease Recovery Tester was used to measure crease-recovery angles [21], with the instrument on setting "A." Each of the values re-

* The mention of trade products in this paper does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

TABLE I. CONDENSATION CATALYSIS BY THE CARBOXYL GROUP AS COMPARED TO THAT OF USUAL CATALYSTS

	15% Dimethylolurea			15% Resloom HP		
	5% Diammonium phosphate*		No added catalyst	5% Monsanto Catalyst AC*		No added catalyst
	Plain cloth	Mercerized cloth†	Carboxymethylated cloth	Plain cloth	Mercerized cloth‡	Carboxymethylated cloth
Resin content (%)	12.4	11.3	11.0	10.9	11.8	14.6
Breaking strength retained (%)	64.3	67.7	86.3	68.8	65.0	82.9
Crease-recovery (degrees)	134	134	121	138	136	140

* Percentage based on weight of resin.

† Control cloth, treated with 15% dimethylolurea without catalyst, had a resin content of 5.0%, breaking strength retention of 87.9%, and crease-recovery of 104°.

‡ Control cloth, treated with 15% Resloom HP without catalyst, had a resin content of 4.9%, breaking strength retention of 88.6%, and crease-recovery of 100°.

ported is the average of five determinations warpwise after the samples had been laundered once.

The resin content of the cloth was approximated by weight gain since the values thus obtained were found to be in close agreement with those actually determined by stripping with 1.5% *ortho*-phosphoric acid containing 5% urea at 80°C for 30 min. [19].

The methods of the American Society for Testing Materials [1] were used for determining breaking and tear strengths and abrasion-resistance. Breaking strength and abrasion-resistance tests were run on specimens ravelled to 80 threads; tear strength was determined by the tapezoid tear test method. The samples were laundered in a reversing type wash wheel with a solution containing 0.5% castile soap and 0.2% sodium carbonate at 140°F for 15 min.

Experimental Procedure and Results

The experimental plan was to establish in preliminary work the effectiveness of resin condensation by the carboxyl group; to compare the catalytic action with that of a commercial catalyst; and to investigate the effects of varying the degree of substitution and of varying the concentration of resin on the properties of the treated cloth. Finally, the important physical properties of treated modified cloth and of treated mercerized cloth were tested and compared.

Condensation Catalysis by the Carboxyl Group

Preliminary.—Samples 10 in. square of plain and mercerized cotton cloth were impregnated with aqueous solutions of dimethylolurea, with diammonium phosphate as catalyst, and Resloom HP, with Monsanto Catalyst AC. Carboxymethylated cotton cloth with a substitution of 0.033, or about one carboxymethyl group per 30 anhydroglucose units, was treated with the same creaseproofing resins without added catalyst. All samples were dried at 100°C for 6 min., cured at 144°C for the same length of time, and laundered.

The results (Table I) show that the carboxyl group is an effective catalyst in condensing the resins. This is especially true of Resloom HP, the melamine-type resin, which was therefore used in subsequent experiments.

It was evident that the partially carboxymethylated fibers had been sufficiently swollen by the modification treatment to allow the resin-former to enter without difficulty. A microscopical study of cross sections of resin-treated carboxymethylated cloth showed by staining that complete penetration of fiber walls occurs with no resin deposited on the outside of the fibers.

Comparison with a commercial catalyst.—Cloth carboxymethylated to 0.067 substitution (about one carboxymethyl group per 15 anhydroglucose units) was treated with 10%, 18%, and 26% Resloom HP solution. Mercerized cloth was treated with the same concentrations of solutions to which 5% Monsanto Catalyst AC (based on weight of resin) had been added. The wet pickup, crease-recovery, and resin content of the treated materials, after curing and after laundering, are given in Table II.

Apparently, the carboxyl group was sufficiently acidic to condense the resins *in situ*, without the need of an added catalyst. The high absorptive quality of the carboxymethylated cloth resulted in greater wet pickup of resin solution than that obtained with the mercerized cloth. An apparent substantive effect of the carboxymethylated material on the resin was evidenced by the removal of larger amounts of resin from solution than would be expected from the percentages of the solutions used.

Effect of varying degree of substitution.—The experiment just described demonstrated the effective catalytic action of the carboxyl group in cloth with a

TABLE II. COMPARISON OF CREASE-RESISTANCE OF RESIN-TREATED MERCERIZED AND CARBOXYMETHYLATED CLOTH

Resloom HP solution (%)	Cloth	Resin content: Wet pickup (%)	After curing (%)	After laundering (%)	Crease-recovery (degrees)
10*	Mercerized	97.7	9.7	9.4	123
10†	Carboxymethylated	98.9	13.9	13.9	122
18*	Mercerized	95.2	15.0	13.0	132
18†	Carboxymethylated	104.4	19.7	18.5	126
26*	Mercerized	101.2	20.2	18.1	116
26†	Carboxymethylated	106.2	22.7	21.3	136

* Containing 5% Monsanto Catalyst AC (based on weight of resin).
† Without added catalyst.

TABLE III. EFFECT OF CARBOXYMETHYL SUBSTITUTION ON CONDENSATION CATALYSIS

Carboxymethyl substitution of cloth*	18% Resloom HP: Resin content: Wet pickup (%)	After curing (%)	After laundering (%)	Crease-recovery (degrees)	22% Resloom HP: Resin content: Wet pickup (%)	After curing (%)	After laundering (%)	Crease-recovery (degrees)	26% Resloom HP: Resin content: Wet pickup (%)	After curing (%)	After laundering (%)	Crease-recovery (degrees)
0.024	95.4	15.4	10.8	121	96.2	17.6	13.3	128	96.8	19.3	15.0	134
0.032	94.4	15.5	12.5	125	95.6	18.0	15.3	138	97.8	19.7	16.7	138
0.037	97.1	16.9	15.3	129	96.6	18.5	16.1	135	98.1	19.8	18.8	136
0.048	97.5	16.7	15.7	136	99.1	19.1	17.8	133	99.7	20.1	20.0	147
0.067	100.9	17.6	17.0	138	102.9	20.4	19.8	140	108.1	22.6	22.0	134

* Degree of substitution is expressed as the ratio of carboxymethyl groups to anhydroglucose units.

substitution of 0.067. To determine the effect of varying the substitution, cloth samples were carboxymethylated to five degrees of substitution: 0.024, 0.032, 0.037, 0.048, and 0.067. Three samples of each group were treated with 18%, 22%, and 26% solutions of Resloom HP, and the usual tests were made after curing and after laundering.

The results (Table III) show that the wet pickup of cloth increases as the carboxymethyl substitution increases, and that with a higher substitution a larger amount of condensed resin is retained after laundering, the latter most probably being due to the high efficiency of the built-in catalyst. Crease-recovery angles, ranging from 121° to 147°, were high for cotton—samples of six commercially resin-treated cotton materials tested at this laboratory showed an average crease-recovery of only 110°. Launderability of resin-treated carboxymethylated cloth was very good, samples of the material withstanding as many as five washings in 0.5% soap and 0.2% sodium carbonate solution without seriously affecting the resin-retention or crease-resistance. Ordinarily, three launderings will remove 25% of the resin applied [22]. A substitution range of 0.067–0.037 (one carboxymethyl group per 15–30 anhydroglucose units) had the best catalytic effect, giving the most efficient resin cures while maintaining a pleasant hand.

In another experiment, resin-treated cloth with carboxymethyl substitution above the range shown in Table III had a harsh, stiff hand.

Effect of varying the concentration of resin.—Cloth of 0.067 substitution, within the range considered optimum for condensation of resin, was treated with Resloom HP in concentrations of from 6% to 26%. The results (Table IV) show that with wet pickups of from 87% to 99%, crease-recovery angles range from 101° to 144°. According to information contained in most commercial bulletins describing creaseproofiing resins, wet pickups of 50%–75% give the best crease-recovery. It is possible that if lower pickups had been obtained, corresponding improvements in crease-recovery would have resulted.

TABLE IV. EFFECT OF RESIN CONCENTRATION ON THE CREASE-RESISTANCE OF CARBOXYMETHYLATED COTTON

Resloom HP solution (%)	Resin content: Wet pickup (%)	After curing (%)	After laundering (%)	Crease-recovery (degrees)*
6	87.3	8.4	8.4	101
10	91.3	12.1	11.1	115
14	97.3	16.3	15.0	129
18	99.0	18.7	16.8	131
22	95.7	19.0	16.9	132
26	98.2	20.9	19.1	144

* Crease-recovery before resin treatment was 88°.

TABLE V. CHARACTERISTICS OF RESIN-TREATED MERCERIZED (*M*) AND CARBOXYMETHYLATED (*C*) CLOTH

Resin content* (%)		Breaking strength (lbs.)		Tear strength (lbs.)		Abrasion-resistance (cycles)		Crease-recovery (degrees)	
M	*C*	*M*	*C*	*M*	*C*	*M*	*C*	*M*	*C*
0	0	44.8	43.5	3.4	3.7	1259	1113	81	78
11.37	13.13	44.8	46.5	2.6	2.7	236	441	128	123
14.52	17.17	45.6	45.8	2.4	2.8	188	300	127	128
16.81	19.44	44.3	45.6	2.3	2.7	159	235	136	125
21.20	20.94	47.2	46.4	2.5	2.6	129	280	130	129

* Determined by stripping with 1.5% phosphoric acid and 5% urea at 80°C for 30 min.

However, on the laboratory equipment used in these experiments it was impossible to get pickups lower than 80% on the 80-square cloth used.

Characteristics of Resin-Treated Cloth

Samples 1 yd. square of carboxymethylated cloth treated with Resloom HP and mercerized cloth treated with the resin solution containing an added catalyst were tested for crease-recovery, breaking strength, tear strength, and abrasion-resistance (Table V). The results indicate that for equal amounts of resin the carboxymethylated cloth has equivalent crease-recovery and breaking strength, slightly higher tear strength, and approximately twice the abrasion-resistance of mercerized cloth. An important difference was that the mercerized samples with high resin contents had a stiff, harsh hand, which was not the case with the carboxymethylated cloth.

Resin-treated, modified cotton also exhibited resistance to ordinary cotton dyes. It resisted such direct cotton dyes as Solantine Blue 4GL (Prototype No. 26) and Triazol Fast Red B (C. I. No. 382), giving a bleached, white appearance after removal from the dye bath and washing. It was possible, however, to carboxymethylate cloth which had been previously dyed with an alkali-resistant dye without affecting its color [7] and then to treat it with resin to impart crease-resistance.

Summary and Conclusions

Two properties of partially carboxymethylated cotton—high swellability and acidity of the carboxyl group—have been utilized in the production of crease-resistant cloth with urea and melamine formaldehyde resins. In general, the modified, resin-treated cotton gives products which are superior in hand, abrasion-resistance, and most of the other important physical properties to unmodified cotton cloth given the same resin treatments.

The condensation catalysis by the carboxyl group proved effective in that the higher the degree of carboxymethyl substitution, the greater the resin pickup and the greater the resin retention after laundering.

Varying the concentration of resin revealed that the carboxymethylated cotton cloth had a higher capacity for the crease-proofing resins and exhibited much less change in hand than the unmodified cloth with equivalent amounts of resin.

Acknowledgment

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The Sorption of Synthetic Surface-Active Compounds by Textile Fibers*

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Abstract

Data are given relating to the sorption of a variety of surface-active compounds from aqueous solution by cotton, viscose rayon, acetate rayon, nylon, and wool fibers. In general, cationic compounds were found to be sorbed to the greatest extent and nonionic compounds the least, the anionic compounds occupying an intermediate position. The addition of sodium sulfate to solutions of sodium alkyl sulfates resulted in an increase in the sorption of the latter compounds in every case. The sorption of nonionic di-isobutyl cresol-ethylene oxide compounds was found to decrease slightly with increasing length of the polyethylene oxide chain over the range studied. Sorption is attributed primarily to the hydrophilic-hydrophobic nature of the surface-active molecules or ions, micelles taking little part in the sorption process, although there is some evidence that positively charged micelles of cationic compounds are sorbed to a slight extent. The degree of sorption may also be influenced by superimposed effects of electrostatic interaction, electrophoretic charges, and the presence of chemcially reactive groups in the fibers. Wide variations were found in the sorption capacities of the different fibers, and the arrangement of the fibers in order of increasing sorption varied with each type of surface-active compound studied.

THE SORPTION of surface-active compounds at soil-solution and fiber-solution interfaces is believed to be an important factor in textile detergency [1, 14, 22, 23]. In connection with studies in the latter field, data have been obtained relating to the sorption of soaps [16, 20] and synthetic surface-active agents [7] by carbon black, representing an important constituent of natural soil, and to the sorption of soaps by textile fibers [21]. The present paper presents similar data for the sorption of a variety of synthetic surface-active compounds by some of the more common textile fibers.

While considerable work in this field has been reported [1, 2, 3, 7, 9, 12 ,18], experimental conditions and methods have varied widely, and each author has dealt with only a relatively few fibers and/or compounds, with the result that a comprehensive comparison of data for the various fibers and compounds has not been possible. Harris [6] has given a review of the literature, and has pointed out that variations in published data may be attributed largely to lack of uniformity or lack of definition of experimental conditions. In the present work experimental condi-

* Some of the material reported in this paper was presented at the Third Canadian Textile Seminar, Queen's University, Kingston, Ontario, Sept. 11–13, 1952.

tions and analytical techniques were carefully standardized and maintained constant throughout so that direct comparisons of the data for the various compounds and fibers would be possible.

Materials

The fibers studied included cotton, wool, and bright and delustered forms of viscose rayon, acetate rayon, and nylon. The sources, characteristics, and preliminary treatment of these fibers have been given previously [21]. It might be pointed out that in the preparation of the fibers for the sorption determinations, all contact with soap or other surface-active agents was carefully avoided.

Three classifications of surface-active compounds were studied: anionic, cationic, and nonionic.

In the anionic group, a series of sodium alkyl sulfates having alkyl chains containing from 12 to 18 carbon atoms were prepared from lauryl, myristyl, cetyl, and stearyl alcohols by the method of Lottermoser and Stoll [8]. The crude products were recrystallized repeatedly from absolute alcohol, and were finally dried to constant weight *in vacuo* at 56°C. Three compounds derived from typical commercial products were also included. These were as follows: *A*, dodecyl benzene sodium sulfonate; *B*, a sodium sulfated salt of gylcerol monolaurate; and *C*, an oleic acid derivative of sodium methyl taurate. Compounds *B* and *C* were obtained by refluxing the commercial product with absolute alcohol, filtering off the insoluble material (largely sodium sulfate), and allowing the residue to crystallize. The product was recrystallized once from fresh absolute alcohol, and was dried to constant weight *in vacuo* at 56°C. Compound *A* would not crystallize from alcohol, but since it was stated by the manufacturer to contain practically 100% active ingredient, it was used as received after drying to constant weight.

In the cationic group, commercial preparations of cetyl trimethyl ammonium bromide (80% active ingredient, remainder largely sodium bromide) and cetyl pyridinium bromide (75% active ingredient) were selected as representing the two major types. These materials were used as received, the concentration of solutions being expressed in terms of the active ingredient.

The work with nonionic compounds was confined to a series of three di-isobutyl cresol-ethylene oxide condensation products which were specially prepared for this work by a commercial manufacturer. The molar ratios of di-isobutyl cresol to ethylene oxide in these compounds were 1 : 10, 1 : 15, and 1 : 20, and since they were stated to contain 100% active ingredient, they were used as received.

It is fully realized that the above list does not begin to cover the vast range of surface-active compounds on the market, but in order to keep the magnitude of the work within reasonable limits, it was necessary to make a selection, and an attempt was made to include those compounds which would be representative of the major types available. As will be shown later, there is a similarity in the sorptive behavior of compounds in any one group, and hence it is probable that little additional knowledge would be gained by a more extensive coverage of the field.

Methods

After conditioning for at least 24 hrs. at 70° ± 2°F and 65 ± 2% R.H., a 6.000-g. sample of fiber was weighed and transferred to a 200-ml. vacuum bottle, which was then placed in an oven maintained at the desired working temperature for 15–20 min. Then 150 ml. of detergent solution adjusted to the desired temperature and initial concentration were added, and the bottle was stoppered and shaken in a mechanical shaking machine for 30 min.* After shaking, the solution was immediately poured off, and an aliquot was taken for analysis.

The concentrations of the anionic solutions were determined by Epton's method [4], employing the modification suggested by Weatherburn [19]. The concentrations of the cationic solutions were determined by adding a measured excess of 0.1% sodium lauryl sulfate solution to the aliquot of cationic solution, and back-titrating the residual anionic compound by the above method.

The concentrations of nonionic solutions were determined by the method of Oliver and Preston [13]. Since this is a gravimetric method, the data were obtained in weight units and were subsequently converted to molar units by employing the theoretical molecular weights of the various compounds.

The moisture contents of the various fibers were determined by drying weighed samples to constant weight at 105°C and reweighing.

* Preliminary experiments indicated that longer shaking periods resulted in only a slight increase in sorption. While it is admitted that true equilibrium was probably not established in 30 min., it was felt that a sufficiently close approach to equilibrium was obtained to be adequate for the comparative data required.

The sorption of a surface-active compound is given by the equation

$$X = \frac{2.5\ (C_o - C)}{100 - A},$$

where X = sorption (millimoles of compound per gram of dry fiber), C_o = concentration of solution before contact with fiber (millimoles per liter), C = concentration of solution after contact with fiber (millimoles per liter), and A = moisture content of conditioned fiber (%).

No correction was made for the selective sorption of water from the detergent solutions by the fibers, it having been shown previously [21] that, under the experimental conditions employed, this has a negligible effect on the sorption data.

Comparison of data for the bright and delustered forms of viscose, acetate, and nylon fibers indicated that the delustered fibers gave slightly higher sorption values than the bright fibers in every case, but the mean difference was only about 6×10^{-4} mM/g. Consequently, in order to simplify the graphs, the average values for bright and delustered forms of the same fiber were plotted.

Results and Discussion

Anionic Compounds

The sorption data for the series of sodium alkyl sulfates at an initial concentration of 3.0 mM/l. are given on the left-hand side of Figure 1.* (3.0 mM/l. is equivalent to 0.086%, 0.095%, 0.103%, and 0.112% for the C_{12}, C_{14}, C_{16}, and C_{18} compounds, respectively.) The measurements were made at a temperature of 50°C for the C_{12}, C_{14}, and C_{16} compounds, and at 70°C for the C_{18} compound since the latter was not sufficiently soluble at 50°C.

The fibers may be arranged in the following order of increasing sorption: cotton, viscose, nylon, acetate, and wool, except that with sodium stearyl sulfate the relative position of nylon and acetate are reversed. The general level of sorption is somewhat lower with the sodium alkyl sulfates than with the sodium soaps of corresponding chain length [21], and the arrangement of the fibers in order of increasing sorption is not the same, the most marked difference occurring in the case of viscose, which sorbed a relatively small amount of alkyl sulfate and a relatively large amount of soap.

It may be seen that the sorption curves for cotton and viscose fibers are similar, maximum sorption being obtained with the C_{16} compound. The curve for acetate is also similar, except that maximum sorption occurs with the C_{14} compound. The curves for wool and nylon fibers differ from those of the cellulosic fibers in that the sorption of the C_{16} compound is lower than that of the C_{18} compound.

A similar series of measurements was made in which the initial solutions contained an amount of sodium sulfate equal to 1½ times the weight of sodium alkyl sulfate. This corresponds to a formulation containing, on a dry basis, 40% surface-active material and 60% sodium sulfate. These data are shown on the right-hand side of Figure 1. The presence of sodium sulfate resulted in an increase in sorption in every case, but the same order of reactivity of the fibers was maintained, except that with both the C_{16} and C_{18} compounds the relative positions of acetate and nylon were reversed. The effect of added sodium sulfate appears, in general, to be greater with the lower members of the series, with the result that the maximum sorption tends to occur at a lower chain length.

It is well known that surface-active compounds owe their activity to the dual nature of their mole-

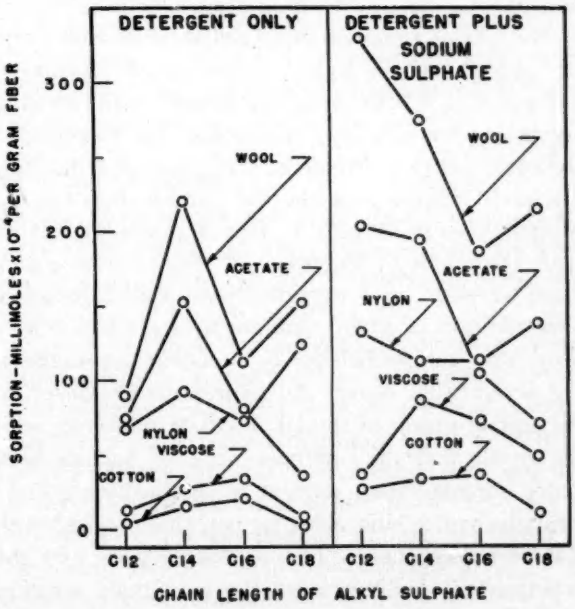

FIG. 1. *Sorption of sodium alkyl sulfates by various fibers.*

* The lines joining the experimental points in Figures 1–4 have no physical significance, but their use provides a convenient method of designating the points and for showing differences in sorptive behavior.

cules—*i.e.*, the latter consist of a hydrophilic or polar constituent and a hydrophobic or nonpolar constituent. This property causes the molecules to accumulate at surfaces and interfaces, and results in the lowering of surface and interfacial tensions. It has also been postulated by Griffin [5] and others that the effectiveness of a surface-active compound for any particular use—*e.g.*, wetting, emulsification, detergency, etc.—depends upon a balance between the hydrophilic and hydrophobic tendencies of these polar and nonpolar constituents of the molecule, and, furthermore, that a different state of balance is required for maximum effectiveness with respect to each of these uses.

It is probable that the inherent polar-nonpolar characteristics of surface-active molecules, which cause them to concentrate and to become oriented at interfaces, are also primarily responsible for their sorption on textile fibers, and it seems reasonable to suppose that the degree of such sorption is likewise dependent upon the state of balance of the surface-active molecule. This could explain, in part at least, the differences in sorptive capacity of the various fibers, since each type of fiber varies in surface properties according to its physical and chemical structure, and might be expected to require a different state of balance of the surface-active molecule in order to obtain maximum sorption.

The application of this concept of hydrophilic-hydrophobic balance to numerical data is hampered by the lack of a method of quantitative measurement, or, indeed, of an exact definition of "balance"; nevertheless, it is believed that certain qualitative observations are justified. Referring, for example, to the curve for the sorption of sodium alkyl sulfates by viscose in Figure 1, it may be inferred that the C_{16} compound is at or near a state of optimum balance with respect to the sorption on viscose since maximum sorption was obtained with this compound. The addition of sodium sulfate to the solution may upset this state of balance by reducing the solubilizing action and, hence, the hydrophilic tendency of the sulfate group of the alkyl sulfate molecule, with the result that the optimum state of balance and, hence, the maximum sorption is obtained with a less strongly hydrophilic nonpolar constituent—*i.e.*, with a shorter alkyl chain. This is in accordance with the experimental findings since the maximum sorption on viscose in the presence of added sodium sulfate was obtained with the C_{14} compound.

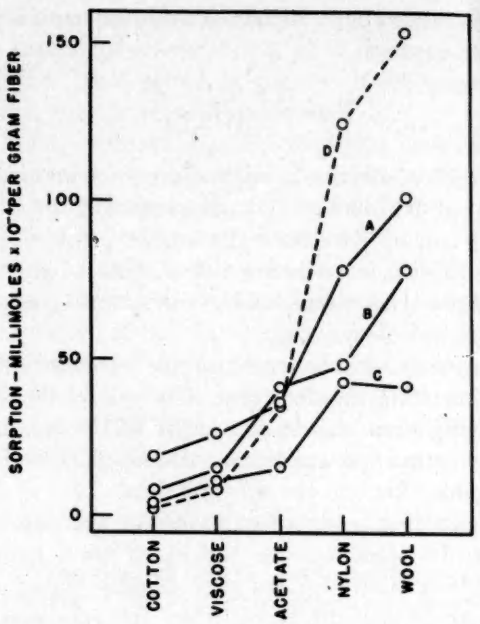

FIG. 2. *Sorption of various anionic compounds by fibers.* A—*Dodecyl benzene sodium sulfonate.* B—*Sodium sulfated salt of glycerol monolaurate.* C—*Oleic acid derivative of sodium methyl taurate.* D—*Sodium stearyl sulfate.*

It is not to be inferred that the sorptive behavior of the fibers and surface-active compounds can be explained entirely on the basis of hydrophilic-hydrophobic balance, but it is believed that this is one contributing factor in a most complex mechanism. As Harris [6] has pointed out, other factors, such as electrophoretic charge, degree of ionization, and the presence of chemically reactive groups, probably play an important part in the sorption mechanism. For example, the higher sorption of sodium stearyl sulfate on nylon and wool cannot be explained on the basis of the foregoing concepts, but it could perhaps be related to the presence of chemically reactive groups in these fibers.

The sorption data for the anionic compounds derived from commercial preparations are shown in Figure 2. The measurements were made at an initial concentration of 0.1% and at a temperature of 50°C. The curve for sodium stearyl sulfate is included for comparison. It may be seen that, in spite of wide variations in chemical constitution, the sorption curves for these four compounds are remarkably similar, the principal deviation being a somewhat higher sorption of sodium stearyl sulfate on nylon and wool.

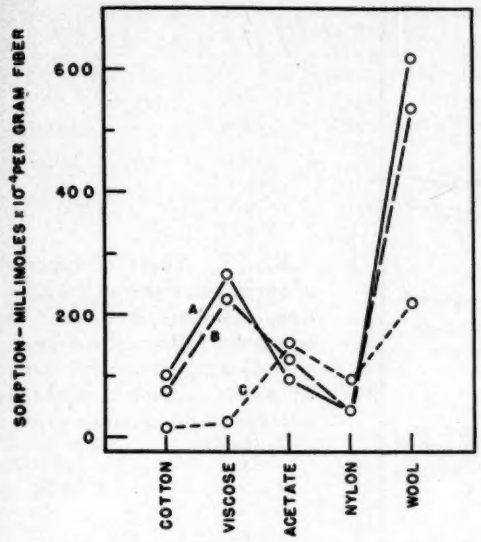

FIG. 3. *Sorption of cationic compounds by fibers.* A—*Cetyl trimethyl ammonium bromide.* B—*Cetyl pyridinium bromide.* C—*Sodium myristyl sulfate.*

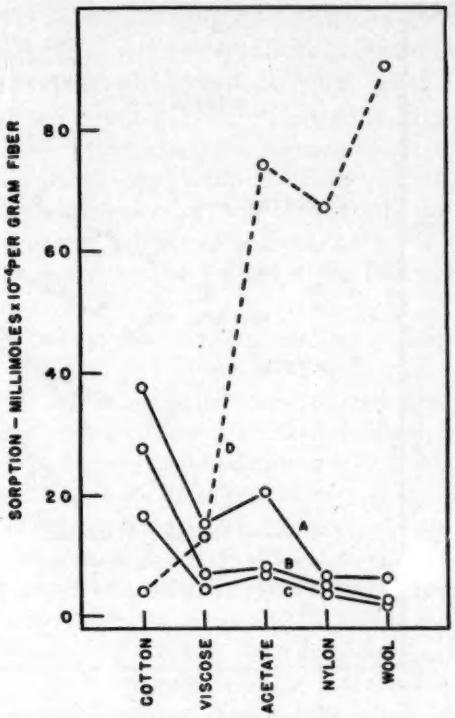

FIG. 4. *Sorption of nonionic compounds by fibers. The molar ratios of di-isobutyl cresol to ethylene oxide were as follows:* A—*1:10;* B—*1:15;* C—*1:20. Curve* D—*Sodium lauryl sulfate.*

Cationic Compounds

The sorption determinations of the two cationic compounds were made at a temperature of 50°C and an initial concentration of 0.1% active ingredient. The results are given in Figure 3; the curve for sodium myristyl sulfate is also included. It may be seen that the sorption characteristics of the two cationic compounds are very similar, but differ considerably from those of the sodium myristyl sulfate. Since the latter compound was, on the whole, sorbed to a greater extent that the other anionic compounds studied, it is obvious that the sorption of the cationic compounds is, in general, much higher than that of the anionic compounds.

It has been shown [11] that all of the fibers included in the present study, when immersed in neutral aqueous solution, exhibit negative electric charges of varying magnitude. It is to be expected, therefore, that these fibers will exert an electrostatic attraction for positively charged ions, and this property is probably largely responsible for the high sorption of the cationic agents. It is obvious, however, that sorption cannot be attributed entirely to electrostatic attraction since the negatively charged ions of the anionic compounds are also sorbed to an appreciable extent. It would seem, therefore, that in the case of anionic compounds the sorption resulting from the tendency of these compounds to concentrate at interfaces is decreased by electrostatic repulsion between fiber and negative ion, whereas in the case of cationic compounds the sorption is increased owing to electrostatic attraction.

Arranging the fibers in order of increasing sorption, the following sequence is obtained: nylon, cotton, acetate, viscose, and wool.

Nonionic Compounds

The sorption of the three nonionic compounds were measured at an initial concentration of 0.1% and at a temperature of 30°C. The results are given in Figure 4.

Comparing these curves with the curve for sodium lauryl sulfate, which is included in Figure 4, it may be seen that the general level of sorption of these nonionic compounds is remarkably low. The higher sorption on cotton and the extremely low sorption on wool are in marked contrast to the behavior of any of the other compounds studied, the order of increasing sorption in this case being: wool, nylon, viscose, acetate, and cotton.

It is apparent that the degree of sorption by all of the fibers decreased slightly with increasing length of

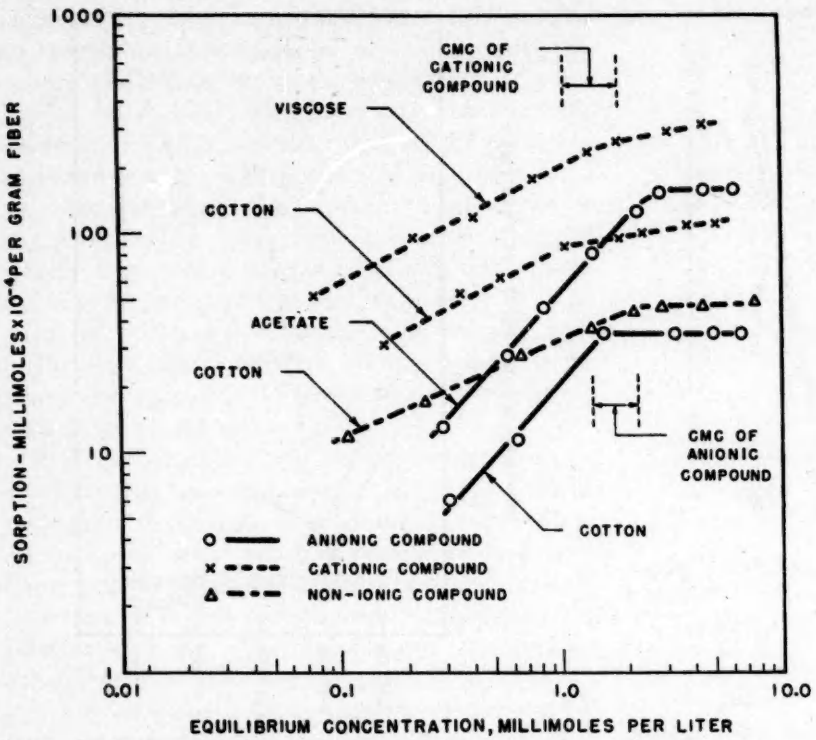

FIG. 5. *Effect of concentration of surface-active compound on sorption. Anionic compound—sodium myristyl sulfate. Cationic compound—cetyl trimethyl ammonium bromide. Nonionic compound—diisobutyl cresol-ethylene oxide, molar ratio 1:10.*

the ethylene oxide chain over the range investigated. This can probably be attributed to variations in the state of hydrophilic-hydrophobic balance of the compounds, since increasing the length of the ethylene oxide chain results in an increase in the hydrophilic tendency of the nonpolar constituent of the molecule while the hydrophobic tendency of the polar part remains unchanged.

Effect of Concentration on Sorption

A limited study of the effect of varying the initial concentration on sorption was carried out, one representative of each of the three types of surface-active compounds being selected together with one or two fibers. Measurements were made at initial concentrations varying from 0.01% to 0.5% and at temperatures of 50°C for the anionic and cationic compounds and 30°C for the nonionic compound. The results are given in Figure 5, in which sorption is plotted against "equilibrium" concentration on logarithmic scales.

The curves appear to be linear up to a concentration which corresponds approximately to the critical micelle concentration.* At this concentration there is a more or less abrupt change in slope, followed by a second linear portion, which, for the anionic compound, is almost parallel to the concentration axis.

According to the well-known Freundlich adsorption isotherm ($X = kC^n$, where X is the quantity sorbed, C is the equilibrium concentration, and k and n are constants), a plot of log X vs. log C should give a straight line. It is apparent that the sorption of the compounds reported in Figure 5 is not capable of representation by this equation over the whole of the concentration range studied. However, Murray [10] has shown that as the total concentration of a colloidal electrolyte is increased above the critical micelle concentration, the concentration of micelles increases very rapidly but the concentration of single long-chain ions quickly reaches a maximum and then remains constant, or even decreases slightly. It may be concluded, therefore, that single long-chain ions are sorbed by the fibers at concentrations both above and below the critical micelle concentration, probably in accordance with the Freundlich equation, and that micelles are sorbed either to a very

* The critical micelle concentration was determined by the method given previously [17], using pinacyanol chloride as indicator for the anionic compound and chlorazol Sky Blue FFS (Color Index No. 518) for the cationic compound. Since this method did not appear to be applicable to nonionic compounds, it can only be concluded by inference that the break in the curve for this compound also corresponds to the critical micelle concentration.

TABLE I. EFFECT OF pH ON SORPTION

Compound	Fiber	Sorption (mM×10⁻⁴/g.) Acid solution	Alkaline solution
Sodium lauryl sulfate	Cotton	11	8
	Viscose	8	1
(3.0 mM/l.; 50°C)	Acetate	83	56
	Nylon	125	68
	Wool	140	139
Sodium myristyl sulfate	Cotton	13	6
	Viscose	52	34
(3.1 mM/l.; 50°C)	Acetate	171	137
	Nylon	156	65
	Wool	300	232
Cetyl trimethyl ammonium bromide	Cotton	81	121
	Viscose	262	318
(0.08%; 50°C)	Acetate	102	122
	Nylon	29	54
	Wool	480	520
Di-isobutyl cresol-ethylene oxide Ratio 1:10 (0.1%; 30°C)	Cotton	54	25

slight extent or not at all. This view is also expressed by Aickin [2] in relation to the sorption of sodium alkyl sulfates by wool.

It has been suggested by Murray [10], Preston [15], and others that single long-chain ions are responsible for surface activity, and that micelles do not concentrate at interfaces because they lack the necessary hydrophilic-hydrophobic properties. It is not surprising, therefore, that the micelles of anionic compounds are not sorbed. Micelles of the cationic compounds, however, are positively charged, and it is to be expected that these will be sorbed to some extent due to electrostatic attraction. This is confirmed by the slight, but significant, slope of the sorption curves for the cationic compound at concentrations above the critical micelle concentration.

Effect of pH of the Solution on Sorption

The sorption of several compounds from acid and from alkaline solutions was measured. The pH of the acid solutions was adjusted to approximately 3.5 with sulfuric acid, and that of the alkaline solutions to approximately 9.5 with sodium carbonate. The results are given in Table I. It may be seen that the sorption of the anionic compounds (sodium lauryl sulfate and sodium myristyl sulfate) on all of the fibers decreased with increasing pH of the solution, while that of the cationic compound (cetyl trimethyl ammonium bromide) increased with increasing pH. This is in accordance with the findings of LeCompte and Creely [7] with respect to the sorption of various types of anionic and cationic compounds on wool.

Neale and Peters [11] have shown that all of these fibers carry negative charges, the magnitude of which increases (negatively) with increasing pH. Amphoteric fibers, such as wool, will of course be positively charged at pH values below their isoelectric points, but this fact does not influence the following discussion.

It has been pointed out in an earlier section of this paper that the high sorption of the cationic compounds is probably related to the electrostatic attraction between the negatively charged fibers and the positively charged surface-active ions. It is evident, therefore, that if the magnitude of the negative charge on the fibers increases with increasing pH, so also will the degree of sorption increase. In the case of anionic compounds, it has been suggested that other forces are responsible for sorption and that these forces operate in opposition to the superimposed electrostatic effects. As the magnitude of the negative charge on the fibers is increased due to increasing pH, this opposing force, or electrostatic repulsion, is also increased, with the result that the degree of sorption is decreased.

On the basis of this explanation it might be expected that the sorption of nonionic compounds would be more or less independent of the pH, but this has not been confirmed experimentally, the sorption of one nonionic compound on one fiber (cotton) showing a definite decrease with increasing pH. In discussing the factors which may influence sorption, Harris [6] made the following statement: "Examination (of nonionic compounds) will show essentially no possibility for ionization, but because these agents form micelles (which can possess definite electrophoretic charges) they possess a weak but nevertheless effective charge." This perhaps offers a plausible explanation for the observed influence of pH on the sorption of nonionic compounds, since the concentration used in these measurements (0.1%) was above the concentration at which the break in the sorption-concentration curve (Figure 5) occurred, and therefore it may be inferred that micelles were present in the solution.

Conclusions

It appears that, of the compounds studied, those in the cationic group are the most strongly sorbed

by the majority of fibers, and the nonionic compounds the least. The anionic compounds occupy an intermediate position, and comparison with previously reported data for sodium soaps [21] indicates that the latter are sorbed to a somewhat greater extent that the synthetic anionics. The apparent sorption of soaps, however, was shown to be due largely to the sorption of hydrolytic fatty acid or acid soap, and under conditions of suppressed hydrolysis the soaps were sorbed to about the same extent as the synthetic anionic compounds.

Considering the fibers, there is little uniformity with regard to their capacity for sorption. Wool, for example, showed a high capacity for the sorption of anionic and cationic compounds, but did not sorb nonionic compounds to any appreciable extent. Cotton, on the other hand, sorbed comparatively small amounts of anionic and cationic compounds, but sorbed more of the nonionic compounds than did any of the other fibers. In general, the arrangement of the fibers in order of increasing sorption varied with each type of surface-active compound studied.

It may be concluded that in a sorption process involving surface-active agents, the primary cause of sorption is the inherent hydrophilic-hydrophobic nature of the molecules, which causes them to concentrate and to become oriented at interfaces. The relative magnitude of the sorption on various types of surfaces is probably influenced by the state of balance of the polar and nonpolar constituents of the molecule. In the case of sorption by textile fibers, the mechanism is rendered more complex by the superimposed effects of electrostatic interaction, of electrophoretic charges, and of the presence of chemically reactive groups in the fibers.

It appears that single unassociated ions (or molecules in the case of nonionizing compounds) of the surface-active agents are primarily involved in the sorption process, although there is some evidence to indicate that the positively charged ionic micelles of cationic agents may be sorbed to a slight extent.

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Electrical Resistance Measurements on Fibers and Fiber Assemblies*

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Abstract

The resistance of single textile fibers and assemblies of these fibers has been studied because of its relation to the effects of static electricity in fibrous materials. An apparatus has been constructed to measure resistances of fibers and assemblies from 10^8 to 10^{16} ohms at specified temperatures and relative humidities. Results of measurements at 30°C on some natural fibers (wool, cotton, hair, silk) and on some man-made fibers (rayon, acetate, nylon, casein) are given for relative humidities from 52% to 85%. Some other synthetic fibers (Orlon, Dacron, Dynel, polyethylene, Velon) have resistances too high to be measured conveniently with the present apparatus. All of the materials measured were found to be ohmic and largely free from polarization effects at voltage gradients up to several hundred volts per centimeter, the limiting values used in the study. The resistivities of all materials tested decreased rapidly with increasing moisture content of the material, the resistivity varying inversely as the 7th to 13th power of the moisture content. Reasonable correlations were found to exist between the resistances of fiber assemblies and the constituents thereof.

Introduction

Static electricity has long bedeviled the textile industry. It led to many problems even when the only fibers processed were the natural ones of cotton, wool, silk, and flax, which are hydrophilic and, consequently, have moderate conductivity. With the advent of the poorly conducting hydrophobic synthetic fibers, such as nylon, Dynel, and Dacron, the effects of static electrification have changed from a mere vexation to a major problem. Both the producer and the user of synthetic fiber products are often seriously troubled by such effects of static electricity as the sparking between two surfaces separated after rubbing, the attraction of dust particles to fabrics, and the repulsion or attraction of charged fabrics. Indeed, the severity of these effects may be a limiting factor in a proposed application. This problem is not confined to the synthetic fibers, for even with the natural fibers a substantial static problem may arise with the present-day increases in processing speeds. Thus, there is considerable practical motivation for a study of electrical processes in fibers in addition to the intrinsic interest of such a study as a problem in chemical physics.

The investigation of static electricity in fibrous materials may be divided into the study of two topics: (*1*) the generation of charge on fibers, and (*2*) the dissipation of that charge. The generation phenomena are difficult to investigate quantitatively until the dissipation phenomena are understood, or at least until they can be measured with meaning. Consequently, it was decided to study first the resistance of fibrous materials, with emphasis on single fibers where the interpretation would not be obscured by the complications of fiber-to-fiber contact, and then to make measurements on fiber assemblies to see how data from single-fiber measurements may be translated into information about assemblies.

The first measurements on single fibers were made on cotton by Slater [12]. Marsh and Earp [6] studied the resistance of single wool fibers as a function of regain. Baxter [1] extended their work by determining the effect of temperature. These papers seem to be the only ones dealing with measurements on single fibers, although there are numerous publications on fiber assemblies such as top, yarn, and cloth. Hearle [5] has given an excellent up-to-date survey of the complete field. The present study is

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concerned with resistance measurements on both single fibers and fiber assemblies of natural and artificial materials. No theoretical explanation of the mechanism of conduction is attempted herein.

Apparatus

Circuit

Textile fibers ordinarily have specific resistivities of the order of 10^6 to 10^{12} ohm-cm.^{2}/cm., and cross-sectional areas of the order of 10^{-6} to 10^{-4} cm.^{2} Hence, samples 1 cm. long have resistances in the range 10^{10} to 10^{18} ohms. The problem of measuring such high resistances turns into the problem of measuring very small currents, whose magnitude depends upon the value of the potential difference applied across the resistor. If this value is limited to 100 or 1000 v., the currents through the fibers considered above may well be less than 10^{-14} amp. Care must then be taken in the choice of instrument and in the design of circuit for measuring fiber resistance.

The measuring circuit (Figure 1) which has been adopted is based on a null-reading electronic electrometer.* Since currents as small as 10^{-12} to 10^{-13} amp. can be detected with the electrometer, resistances up to 10^{15} and possibly 10^{16} ohms may be measured when the impressed potential difference, V_x, is of the order of 1000 v. In the circuit of Figure 1 a variable high-voltage supply puts a known voltage, V_x, across the unknown resistance, R_x. The voltage V_s is adjusted until the electrometer reads zero potential difference across its terminals. In the steady state the current through R_x is equal to the current through R_s, and R_x is given by

$$R_x = (V_x/V_s)\, R_s.$$

This circuit has the following advantages:

(*1*) The only path for the current which leaves R_x is through R_s and the electrometer insulators; but, since the potential difference across the electrometer is zero at balance, the leakage current will be small even if the leakage resistance should happen to be low.

(*2*) The electrometer is used only as a null indicator; therefore, only the roughest of calibrations is necessary, and deviations from linearity of response are of no importance.

(*3*) Only low impedance instruments, with their attendant ruggedness and stability, are necessary for the quantitative readings.

* This circuit was described by Norman [10]. It is closely related to that described by Townsend [14].

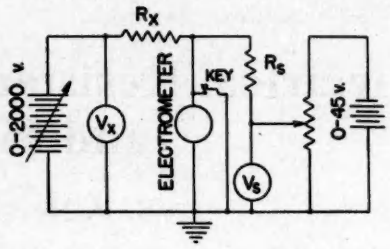

FIG. 1. *Circuit to measure high resistances.*

In practice, the ratio V_x/V_s should not exceed 1000, and it is necessary to have standard resistors up to 10^{12} ohms.* These resistors are available commercially, but in their higher ranges need to be checked regularly because of possible instability or surface contamination. For this purpose, it is well to have a set of resistors—say 10^6, 10^8, 10^{10}, 10^{12} ohms—and to check the higher ones against the lower ones successively in the circuit of Figure 1.

Test Chamber

Since the resistance of most fibers varies strongly with temperature and with moisture content, it is imperative to provide a well-controlled atmosphere. The testing chamber space must be ample for storage of the fibers during conditioning and for measurements on these samples. The chamber must be accessible for insertion of fibers into and removal of fibers from the measuring circuit. The temperature should be controlled to within 0.1°C in order to maintain relative humidity constant within ½% or better. It should be possible to vary the relative humidity between the limits of 5% and 95%, and the temperature between the limits of 0°C and 50°C.

A diagram of the apparatus built to meet these specifications is shown in Figure 2. The test space is enclosed by a galvanized iron tank 12 in. deep by 18 in. wide by 24 in. long, open at the top and covered by a ¼-in. Lucite lid. The tank is set in a thermostatted circulating water bath up to 1 in. from its top. The humidity in the test space is controlled by circulating the enclosed air over flat trays containing saturated salt solutions. Forced circulation is obtained by means of a small externally powered fan. Another sheet of ¼-in. Lucite (not shown in Figure

* In the event that suitable known resistors are not available, R_s may be replaced with a known capacitor. The measurement then is based on the time rate of change of voltage across the capacitor necessary to maintain zero potential difference across the electrometer. For details, see Norman [10].

2) covers the entire water bath to provide a dead-air insulation space between the outside atmosphere and the test chamber. In case the room temperature fluctuates much, it is advisable to add a sheet or two of ½-in. insulating board on top of the Lucite.

Below is a list of the saturated salt solutions used for this work, together with the relative humidities maintained by these solutions at 30°C.

Saturated salt solution	Relative humidity (%)
Potassium chloride	84½
Sodium chloride	75
Sodium nitrite	64
Cobalt chloride	62
Sodium dichromate	52

The humidity values for potassium chloride, sodium chloride, and cobalt chloride at 30°C were taken from O'Brien [11]. The humidity values for sodium nitrite and sodium dichromate were measured within ± 1% by means of a commercial hair hygrometer. Although the absolute values of the humidity were not known more accurately than listed above, the humidity was maintained constant at each point within ± 0.1%, as measured by a Dunmore humidity-sensing element. The temperature within the chamber was controlled at 30° ± 0.05°C.

Components of Measuring Circuit

With the measuring circuit employed, it is necessary to bring into the test space one lead to apply the test voltage, and to bring out of the test space another lead to measure the test current. The in-lead must be able to withstand high voltages, but does not require an exceptionally high leakage resistance. The out-lead, however, is the critical point in the circuit with respect to leakage currents, and has the additional requirement that its capacitance to ground be small. Design difficulties with the in-lead were consequently unimportant; those with the out-lead were met by supporting it by two small Teflon insulators. To keep the capacitance low, the out-lead was made small and the spacing of this lead from other conductors was kept large.

The chief requirements of the sample holders are that they hold numerous samples and permit switching of different samples into the measuring circuit without disturbing the test space. The general arrangement adopted is shown in Figure 2, and a detailed sketch is shown in Figure 3. The fibers are mounted on small brass tabs in a manner to be described below. The upper tabs to which the fibers are attached are held by Phosphor-bronze clips attached to a Lucite disk supported by a vertical brass rod. Fibers as long as 20 cm. can be hung from these disks, although the usual sample length was 1–2 cm. The tabs on the lower ends of the fibers make contact with the out-lead by brushing over the out-electrode when the Lucite disk is rotated. This rotation is effected by turning the upper end of the supporting rod, which projects through the sheet covering the test space. Four of these fiber holders are contained in the test chamber, and each of these holders has

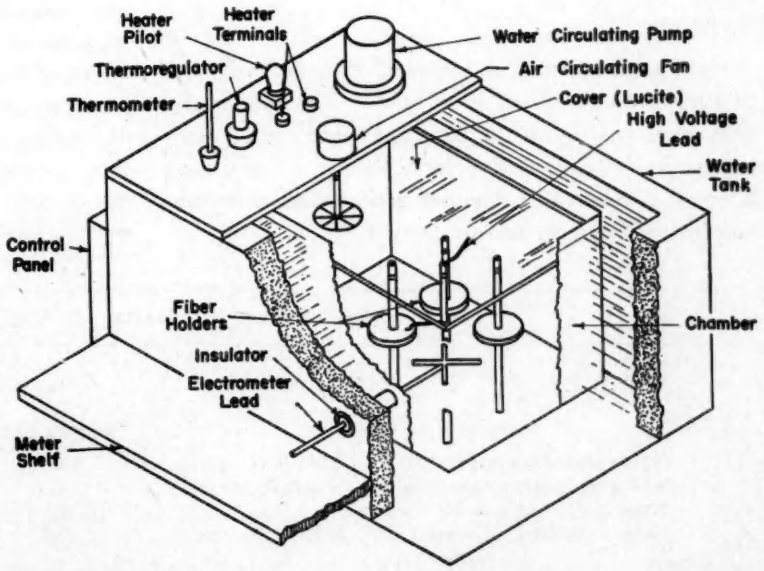

FIG. 2. *Apparatus for the measurement of electrical properties of fibrous materials.*

twelve clips. Contact with the in-lead is provided by a movable Phosphor-bronze brush which touches the clip holding the upper end of the fiber. In order to prevent all the fibers on a holder from becoming charged when the high voltage is applied to one fiber, all fibers are isolated from each other by guard rings drawn with conducting silver paint (Duco 4817) as radial lines on the disk. A Faraday cage isolates the circuit components in the chamber from the air-circulating fan, the saturated salt solutions, and the humidity-sensing element contained in the rest of the test chamber.

The rest of the circuit components are the voltage supplies and meters. These components are supported on a shelf attached to the outside of the water bath.

Measurements on Single Fibers

Materials

Resistance measurements were made on single fibers of the materials listed below.

Man-made fibers	Natural fibers
Acetate	Vegetable
Viscose rayon	Cotton
Nylon	
Orlon	Animal
Dacron	Hair, human
Dynel	Wool, Columbia's
Polyethylene	Wool, B.A.'s
Velon	

Mounting

Each single fiber was mounted on a pair of $\frac{1}{4}$ in. $\times \frac{3}{4}$ in. tabs of 0.005-in. shim brass. The ends of the fiber were placed on the tabs and were coated with conducting silver paint (Duco 4817). The coated fiber ends were then covered with cellulose acetate cement for strength and protection.

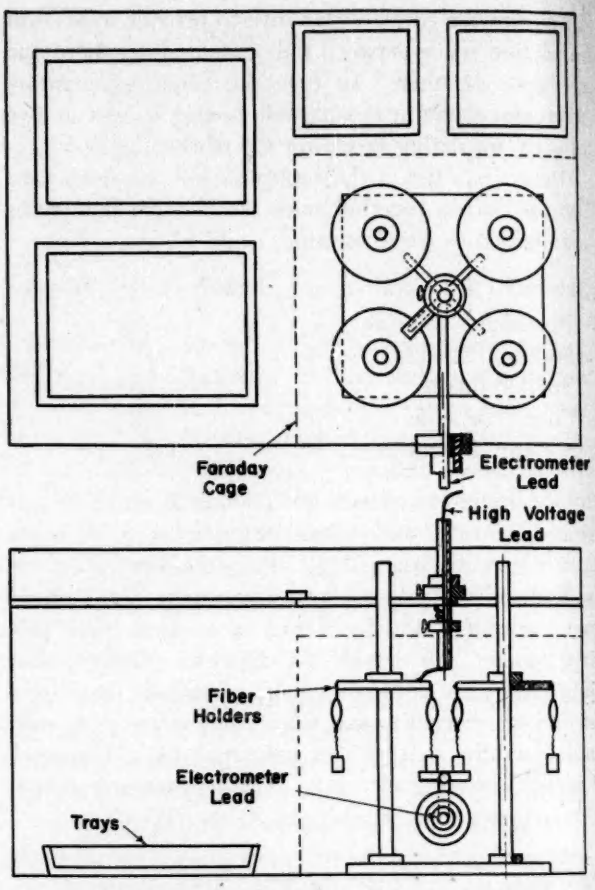

FIG. 3. *Detail of sample holders and test chamber.*

Fiber Preparation

Ordinarily the fibers were washed in several changes of distilled water after mounting. In preliminary tests it was established that washing in organic solvents had no effect on the resistance of fibers, and consequently washing in these solvents was dispensed with. The effect of washing in distilled water is usually to raise the resistance to some terminal value, presumably owing to removal of salts

TABLE I. EFFECT OF WASHING ON FIBER RESISTANCE

Samples	Resistance (10^{12} ohms) Not washed	After 1 washing	After 2 washings	After 3 washings
Nylon monofilament—340 denier, 75% R.H., 1 cm.	—	8.2	9.1	9.1
Nylon monofilament—30 denier, 75% R.H., 1 cm.	—	160	180	180
Wool (58's)—85% R.H., 2 cm.	4.2	14	16	16
Hair—~0.001 in. diameter, 85% R.H., 2 cm.	5.4	5.4	6.3	6.3

on the fiber surface. Table I shows typical results of washing fibers repeatedly in distilled water. It will be noted that the first washing usually causes a large increase in resistance, and that a second or third washing suffices for attainment of the terminal value.

Measuring Technique

After the fibers had been mounted and supported on the disks, they were placed in the test space to condition for several days. To make a measurement, a fiber was positioned between the electrodes, and the test voltage, V_x, was applied with the electrometer grounded. A balancing voltage, V_s, was estimated and applied to that end of the standard resistor, R_s, connected to voltmeter V_s. The grounding key on the electrometer was opened, and the sign and the magnitude of the deflection on the electrometer were noted. The voltage V_s was adjusted accordingly, until the electrometer read zero. When polarization or heating effects were suspected, the applied voltage was reduced to zero, and the fiber was allowed to rest for a few minutes. The voltage was then reapplied to see if there was any change in the reading.

Reproducibility

The day-to-day variability of resistance measurements on the *same* fibers can be evaluated from the data of Table II, where results are given for fibers after one washing. It is seen from this table that after the 3 to 5 days required for establishing equilibrium, the day-to-day variability usually does not exceed 5%.

Fiber-to-fiber variability for specimens drawn from the same sample will depend upon the uniformity of the sample and upon the handling of the specimens. Table III shows typical fiber-to-fiber variability for selected materials. Each sample listed was cut into a number of equal lengths, the resistance measured, and the resistivity computed. One sample was taken for each of three different nominal sizes of nylon filament. Two different samples were taken in the case of human hair, and three different samples in the case of Columbia wool; a single Buenos Aires wool sample is listed also. The agreement in resistivity for each sample is surprisingly good, even with the natural fibers.

Polarization

The polarity of applied voltage had negligible bearing on the measured resistance in those cases where this effect was studied. The resistance changes with time of application of test voltage were negligible for most fibers. With low resistances, of the order of 10^{10} ohms, an increase in resistance with time was observed; it is believed that this increase results from loss of moisture through heating.

Ohmicity

The constancy of resistance with respect to voltage was investigated for both the standard resistors and the fibers. The standard resistors were found to be ohmic within the limits of precision of measurement, about ½%, from 0.01 v. through 100 v. All the fibers studied from 50 v. to 2000 v. were found to be ohmic. Figure 4 shows IR_s (the current, I, through the fiber times a constant, R_s) as a function of the test voltage, V_x, for several fibers. The points are seen to lie very close to straight lines through the origin. With most other fibers the resistance was measured only at 1000 v. and 2000 v., and was found to be constant.

TABLE II. DAY-TO-DAY VARIABILITY OF RESISTANCE MEASUREMENTS ON SINGLE FIBERS

Samples	Resistance (10^{12} ohms) for conditioning times of: 36 hrs.	108 hrs.	132 hrs.	156 hrs.
Viscose filament—~2 denier, 50% stretch, 75% R.H., 1 cm.	0.12 0.11	0.86 0.79	0.80 0.73	0.81 0.75
Viscose filament—~2.5 denier, 75% R.H., 1 cm.	0.69	0.65	0.65	0.65
Viscose filament—~2 denier, 200% stretch, 75% R.H., 1 cm.	0.52	0.47	0.45	0.46
Nylon monofilament—340 denier, 75% R.H., 1 cm.	8.1 8.5	8.1 8.5	8.2 8.6	8.3 8.7
Nylon monofilament—30 denier, 75% R.H., 1 cm.	140 170	140 140	140 130	140 150

TABLE III. SAMPLE-TO-SAMPLE VARIABILITY OF RESISTANCE OF SINGLE FIBERS

Sample	No.	Resistance (10^{12} ohms)	Resistivity (10^9 ohm-cm.^{2}/cm.)
Nylon monofilament—340 denier, 64% R.H., 1 cm.	1	36	12
	2	40	13
	3	36	12
	4	38	12
	5	50	16
	6	39	13
	7	37	12
	8	41	13
Nylon monofilament—30 denier, 64% R.H., 1 cm.	1	1100	32
	2	900	26
	3	900	26
	4	1000	29
	5	1000	29
	6	1000	29
	7	1400	41
	8	1100	32
Nylon tow—3 denier, 85% R.H., 2 cm.	1	480	1.00
	2	460	0.95
	3	490	1.00
	4	460	0.95
	5	480	1.00
	6	480	1.00
	7	480	1.00
	8	460	0.95
	9	520	1.10
	10	440	0.90
	11	480	1.00
Human hair—~0.001 in. diameter, 85% R. H., 2 cm.	A1	7.1	5.7
	A2	7.4	6.8
	A3	6.3	6.2
	B1	4.2	6.2
Wool (Columbia 58's)—85% R.H.; A1, B1, C1, 2 cm.; A2, B2, 1.5 cm.	A1	16	0.095
	A2	12	0.092
	B1	17	0.089
	B2	11	0.075
	C1	10	0.050
Wool (Buenos Aires)—85% R.H., 2 cm.		16	0.087

Length

The effect on resistance of varying the fiber length from 1 cm. to 8 cm. was studied for several types of fibers. The primary purpose of this study was to ascertain the possible effect of contact resistance, inasmuch as ohmicity and uniformity are better established by other tests. Figure 5*a* shows the variation of resistance with length for several high-resistance fibers. The data are fitted within the precision of measurement by straight lines through the origin, and thus there is no indication that the manner of contact has appreciable effect. Figure 5*b* shows similar data for a group of medium-resistance fibers. Except for the 8-cm. lengths, the data are again fitted by straight lines through the origin. At 8 cm. the resistances appear anomalously low, an effect which is possibly explained by insufficient washing of the 8-cm. length. To check this explanation, the test was repeated with thoroughly washed 340-denier nylon. It was then found that the resistance was proportional to length. But, in any event, there is no evidence of an end-effect of more than a few percent, and it is believed that for single fibers of sample length 2–3 cm. and of resistances greater than 4×10^{12} ohms the effects of contact resistance are negligible.

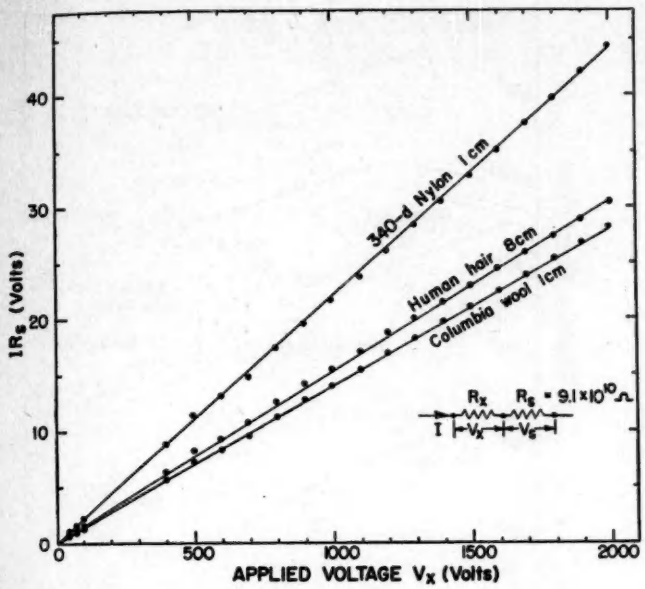

FIG. 4. *Current-voltage relationship, showing ohmicity of single fibers at 85% R.H. and 30°C.*

Diameter

The study of the dependence of resistance upon diameter is one of the most effective means of separating the volume resistivity and the surface resistivity. Unfortunately, not many samples of the same material were available in different diameters. The most extensive sets of samples available were those of nylon and Dynel. However, the Dynel has such a high resistivity that only low-precision measurements are possible with it in the present circuit. Hence, results for nylon only were obtained. Figure 6 is a logarithmic plot of the resistance of some textile nylon fibers against diameter at 30°C and 85% R.H. On this plot the graph for a material of constant finite volume resistivity and infinite surface resistivity would be a straight line of slope -2, and that for a material of infinite volume resistivity and constant finite surface resistivity would be a line of slope -1. The graph for a material with constant but finite surface and volume resistivities would tend to the line of slope -2 at large diameters, and that of slope -1 at small diameters. In Figure 6 the solid line shown is of slope -2, and the experimental points lie close to it. Thus, it is indicated that under the experimental conditions the conduction for nylon filaments in the diameter range 20–200 μ (3–340 denier) is primarily throughout the volume of the material.

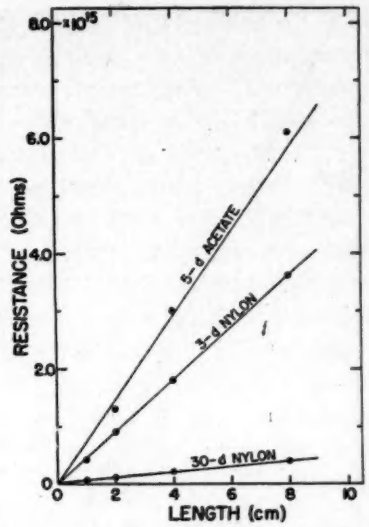

FIG. 5a. *Resistance of single fibers (high resistance) as a function of sample length at 85% R.H. and 30°C.*

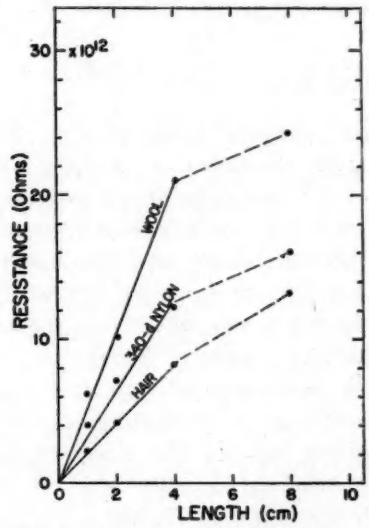

FIG. 5b. *Resistance of single fibers (medium resistance) as a function of sample length at 85% R.H. and 30°C.*

Diameters were measured by micrometer calipers, microscope, or vibroscope [8]. In the case of the vibroscope, the actual quantity measured is the mass per unit length, which is converted into equivalent diameter. For a fiber whose cross section shows slight ellipticity, as is the case with nylon, this equivalent diameter has direct meaning; for a fiber whose cross section differs radically from a circular shape, as is the case with cotton, this equivalent diameter is only a nominal quantity.

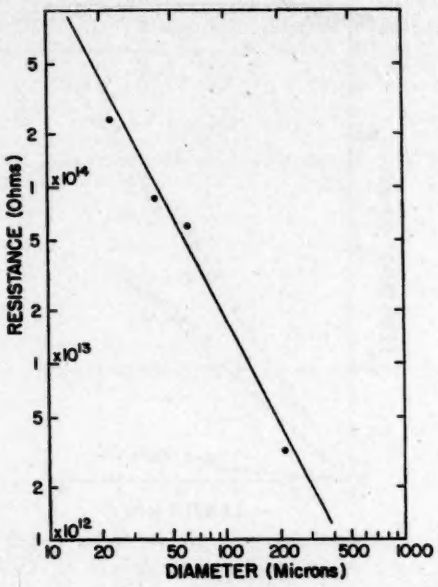

FIG. 6. *Resistance of nylon monofils as a function of diameter at 85% R.H. and 30°C.*

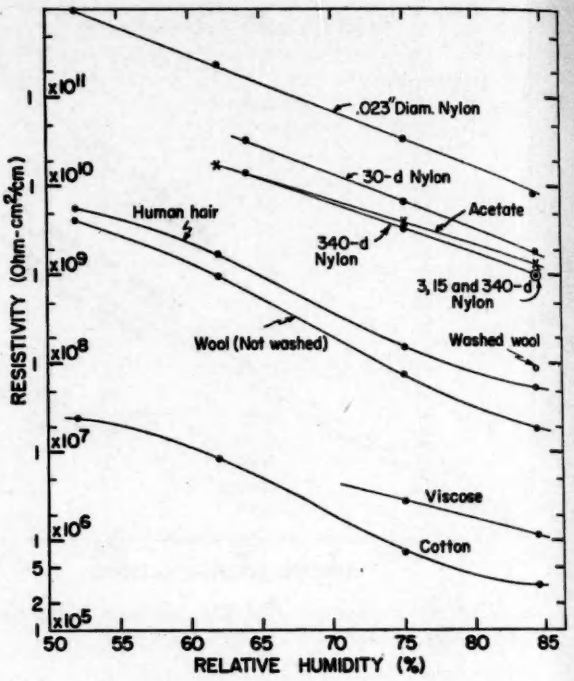

FIG. 7. *Resistivity of single fibers at 30°C as a function of relative humidity.*

Effect of Relative Humidity

Apart from chemical components of the fiber or fiber coating, the variable most strongly affecting the resistivity of fibrous materials is the moisture content. Figure 7 is a semilogarithmic plot of the volume resistivity of various single fibers as a function of relative humidity in the range 52% to 85%. The volume resistivity was computed on the assumption that the surface resistivity is infinite. Figure 8, based on the same original data as Figure 7, is a logarithmic plot of the resistivity against moisture content (on wet basis). The moisture content as a function of relative humidity was obtained from standard sources [2, 4, 7, 13, 15].

Over the range of moisture contents studied, the points in Figure 8 for a given material fall on a nearly straight line. A straight line in this figure satisfies the relation

$$\rho = K' M^{-n},$$

where ρ is the resistivity in ohm-cm.²/cm. and M is the moisture content in percent, calculated as 100 times the weight of moisture divided by wet weight of fiber. Here n and K' are constants. In order to compare the present results with those tabulated by Hearle [5], K' must be multiplied by the fiber density to give Hearle's constant K. Table IV gives the values of n and $[(\log K) - n]$ for the data of Figure 8.

For single fibers the only entry in Hearle's table is that of Marsh and Earp [6] for wool. These workers found a value for n of 17.2, whereas Table IV shows a value of 12.6. A detailed examination of the data shows that the points do not fall exactly on a straight line, and that in the case of the work by Marsh and Earp the steepest portion of the curve has been taken. If this procedure is followed with the present data, a value for n of 16.8 is found, which is quite consistent with the earlier value of 17.2. The value of $[(\log K) - n]$ is not obtainable in the data of Marsh and Earp.

TABLE IV. VALUES OF n AND $[(\log K) - n]$ FOR LOGARITHMIC PLOTS OF SINGLE-FIBER RESISTIVITY AGAINST MOISTURE CONTENT AT 30°C

Material	n	$(\log K) - n$
Acetate	5.8	10.0
Nylon monofilament—340 denier	7.4	7.2
Nylon monofilament—30 denier	8.7	7.3
Nylon monofilament—.023 in. diameter	9.0	7.8
Wool (Columbia 56's)	12.6	10.7
Hair	11.5	11.0
Cotton	7.5	7.0
Viscose rayon	5.3	7.7

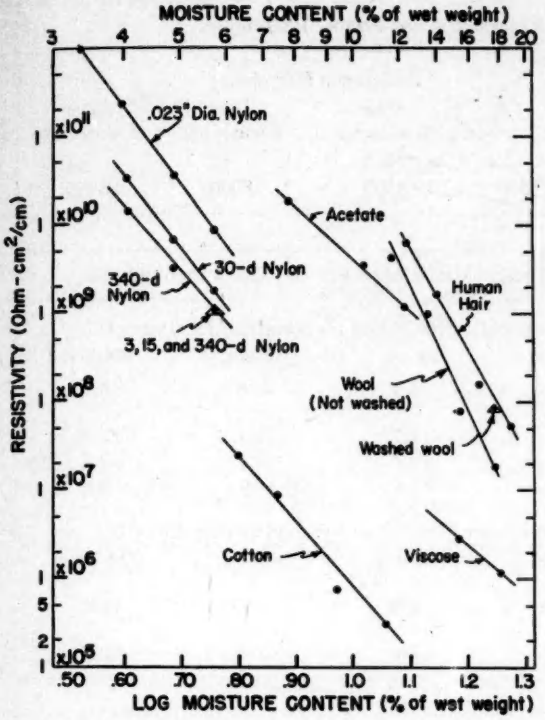

FIG. 8. *Resistivity of single fibers at 30°C as a function of moisture content (wet basis).*

In Figures 7 and 8 it is seen that the 0.023-in. diameter nylon sample, a commercial fishing line, has a resistivity 5 to 8 times higher than that of the textile nylons (340, 30, 15, and 3 denier). Whether this disparity results from differences in polymer composition or differences in processing, plasticization, or surface treatment is not ascertainable at the present time, inasmuch as the processing histories of the samples are not known.

TABLE V. LOWER LIMITS OF RESISTIVITY FOR THE HYDROPHOBIC SYNTHETIC FIBERS AT 85% R.H. AND 30°C

Sample	Resistance (10^{15} ohms)	Resistivity (ohm-cm.²/cm.)
Dynel—80 denier, unoriented, sixteen 2-cm. strands in parallel	10	$>6 \times 10^{12}$
Polyethylene—0.012-in. diameter monofilament, 2 cm.	20	$>7 \times 10^{12}$
Velon—0.008-in. diameter monofilament, 2 cm.	20	$>3 \times 10^{12}$
Orlon—3-denier staple fiber, 1 cm.	20	$>5 \times 10^{10}$
Dacron—3-denier staple fiber, 1 cm.	20	$>5 \times 10^{10}$

The resistivity of single fibers of Dynel, Orlon, Dacron, polyethylene, and Velon were too high to permit accurate measurements to be made. Accordingly, only lower limits of resistivities can be given for these materials, as listed in Table V.

The limiting factor here was the resistance measurement. The maximum value of resistance measurable is about 2×10^{16} ohms, and this value was observed for all the samples under consideration. But, because samples of much smaller cross-sectional area were taken for the Orlon and Dacron, the resistivities calculated for these samples are much lower. Therefore, from these results it cannot be assumed that the resistivities of Orlon and Dacron are necessarily two orders of magnitude lower than those of the other materials. The value given for Dynel is believed to be correct within a factor of 10.

Measurements on Fiber Assemblies

Materials

Resistance measurements were made on the fiber assemblies listed below.

The cuprammonium rayon yarn, and of course the cotton and wool yarns, were spun staple. The other samples were continuous filament.

Materials	Nominal Size
Yarns	
Nylon * (treated)	70 denier
Nylon tire cord	2110 denier
Acetate *	75 and 300 denier
Saponified acetate	30/40
Viscose rayon	150/40, 100/40, 150/90, 150/75
Cuprammonium rayon	350 denier
Casein	321 denier
Cotton	21's
Wool	42's
Raw silk, Japanese white	20/22
Polyvinylchloride	~ 40 denier, 20 filament
Fabrics	
Nylon * (treated)	
Acetate *	

* These materials are standard samples provided by the A.A.T.C.C. Subcommittee on Antistatic Finishes. The nylon sample was treated with a finishing agent of unknown composition.

TABLE VI. EFFECT OF WASHING ON RESISTANCE OF FIBER ASSEMBLIES

Samples	Resistance (10^9 ohms) Not washed	After 1 washing	After 2 washings	After 3 washings
Viscose yarn—150/90, 75% R.H., 1 cm.	—	9.3	15	14
Acetate yarn—300 denier, 85% R.H., 2 cm.	5700	8500	8000	8500

TABLE VII. DAY-TO-DAY VARIABILITY OF RESISTANCE MEASUREMENTS ON FIBER ASSEMBLIES

Yarn samples	Resistance (10^9 ohms) for conditioning times of: 36 hrs.	60 hrs.	84 hrs.	108 hrs.
Viscose yarn—150/90, 75% R.H., 1 cm.	12.6	8.9	8.8	8.9
Viscose yarn—150/75, 75% R.H., 1 cm.	13.8	11.7	11.2	11.5
	12.7	10.8	10.6	10.7
	17.1	14.0	13.6	13.8

Fabric samples	Resistance (10^9 ohms) for conditioning times of: 36 hrs.	108 hrs.	132 hrs.	156 hrs.
Acetate fabric—75% R.H., 0.5 × 2.0 cm.	1320	1400	1410	1420
Nylon fabric—75% R.H., 0.5 × 2.0 cm.	3800	4300	4200	4100

Mounting

The yarn samples were mounted on pairs of brass tabs, in the same fashion as were the single fibers. The fabric samples, which were 0.5 cm. × 2.0 cm. strips, were mounted directly in the upper Phosphor-bronze clips, which had a gripping surface 0.5 cm. wide. For the bottom electrode another Phosphor-bronze clip was used to grip the 0.5-cm. strip of fabric 2.0 cm. from the upper clip.

Sample Preparation

Ordinarily the samples were washed in several changes of distilled water after mounting. Table VI shows typical results of repeated washing in distilled water. It will be noted that, just as with the single fibers, the first washing results in a large increase in resistance, and that two additional washings suffice for attainment of the terminal value.

Measuring Technique

The measuring technique for the assemblies was the same as that for the single fibers.

Reproducibility

The day-to-day variability of resistance measurements on the *same* samples can be evaluated from the sets of measurements given in Table VII. It is seen from Table VII that after the 3 to 5 days required for establishing equilibrium, the day-to-day variability does not exceed 3%.

TABLE VIII. SAMPLE-TO-SAMPLE VARIABILITY OF RESISTANCE OF YARN

Sample	No.	Resistance (10^9 ohms)	Resistivity (10^6 ohm-cm.^{2}/cm.)
Viscose yarn—150/75, 75% R.H., 1 cm.	A1	12	1.3
	A2	14	1.5
	A3	33	3.5
	B1	16	1.7
	B2	15	1.6
	B3	27	2.9

Sample-to-sample variability for specimens taken from the same source will depend upon the uniformity of the material and upon the handling of the material. Table VIII shows typical sample-to-sample variability for viscose yarn. Three equal lengths were cut from each of two yarns, *A* and *B*, of the same type. There is considerable variation between samples, but it is believed that the disparity arises from unevenness in yarn structure and from difference in fiber-to-fiber contact.

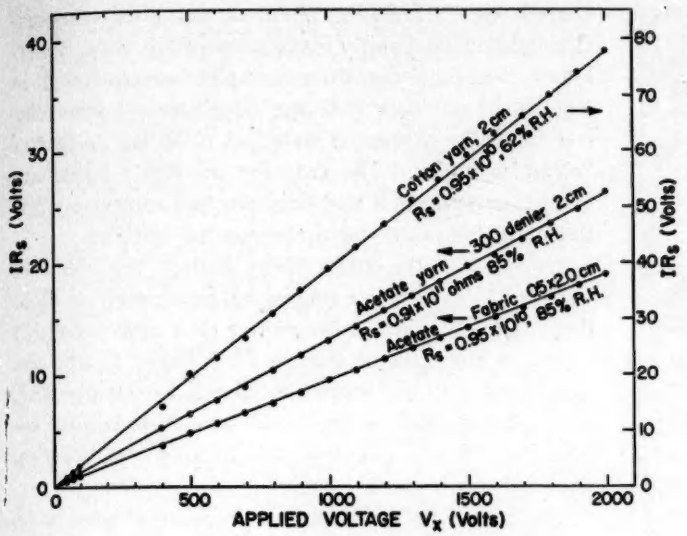
Cotton yarn, 2cm
Rs = 0.95x10^9, 62% R.H.
Acetate yarn 300 denier 2cm
Rs = 0.91x10^11 ohms 85% R.H.
Acetate Fabric .05x2.0cm
Rs = 0.95x10^10, 85% R.H.
IRs (Volts)
APPLIED VOLTAGE Vx (Volts)

FIG. 9. *Current-voltage relationship, showing ohmicity of fiber assemblies at 30°C.*

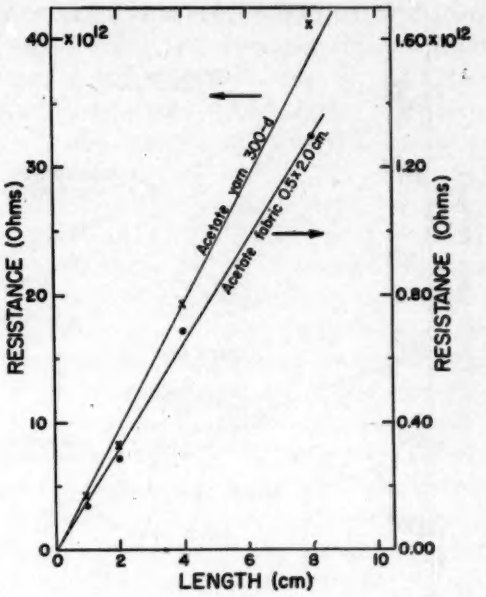

FIG. 10. *Resistance of fiber assemblies as a function of sample length at 85% R.H. and 30°C.*

Polarization

With respect to polarization, the assemblies behaved like the single fibers.

Ohmicity

Samples of cotton yarn, acetate yarn, and acetate fabric were found to be ohmic from 50 v. to 2000 v. Figure 9 shows IR_s (the current, I, through these samples times a constant, R_s) as a function of the test voltage, V_x. The points are seen to lie closely about a straight line through the origin. With most other samples the resistance was measured only at 1000 v. and 2000 v., and was found to be constant.

Of particular interest are the measurements on cotton yarn, as shown by the steepest line in Figure 9. The resistance is seen to be almost exactly ohmic, a finding in apparent opposition to the results of Evershed [3] and Murphy [9]. However, it is to be emphasized that in the present experiments the applied voltage was maintained for at least 30 sec., and usually several minutes; therefore, the data of Figure 9 refer to resistances obtained in the steady state, where polarization has reached an equilibrium value, whereas other workers usually dealt with measurements under nonequilibrium conditions.

Length

The variation of resistance with changes in sample length from 1 cm. to 8 cm. was studied for one yarn only—a 300-denier acetate yarn. The results obtained are shown in Figure 10. There is no evidence of any important end-effect, since the points fall fairly closely about a straight line through the origin.

The effect of sample length from 1 cm. to 8 cm. was studied for an acetate fabric. Figure 10 shows the dependence of resistance on length. Again, there is no evidence of any important end-effect.

Effect of Relative Humidity

Figure 11 is a semilogarithmic plot of the volume resistivity of various fiber assemblies as a function of relative humidity in the range 52% to 85%. The volume resistivity has been computed on the assumption that the fiber and yarn cross-sectional areas are equal to the lineal density divided by the fiber density, the surface resistivity being taken as infinite. The resistivities of the fabrics have been calculated on the assumption that the effective cross-sectional area of the fabrics is equal to the sum of the cross-sectional areas of the yarns which run parallel to the direction of the applied voltage. The validity and significance of such an assumption will be discussed later for the case of the acetate fabric. Figure 12, based on the same original data as Figure 11, is a logarithmic plot of the resistivity against moisture content (on wet basis). The data for casein fiber and saponified acetate are not given in Figure 12. Even though the nylon fabric and yarn samples were

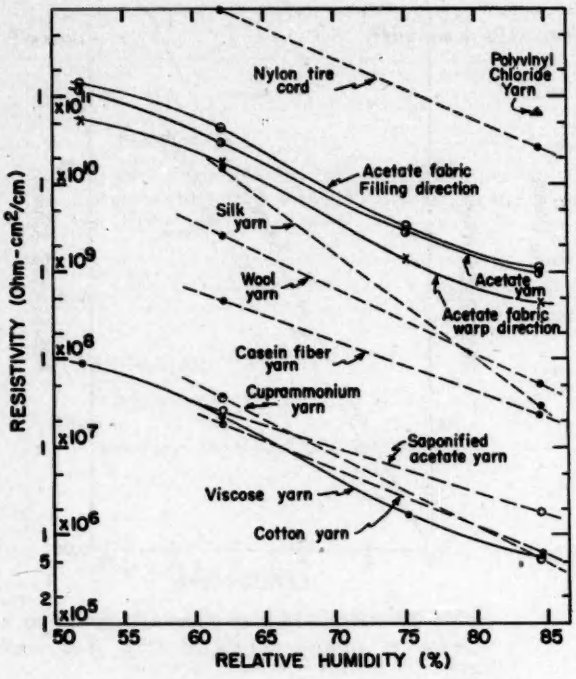

FIG. 11. *Resistivity of fiber assemblies at 30°C as a function of relative humidity.*

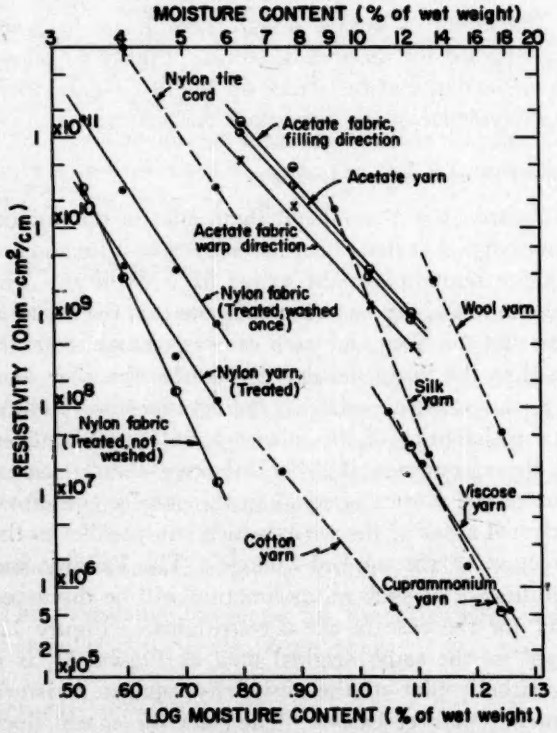

FIG. 12. *Resistivity of fiber assemblies at 30°C as a function of moisture content (wet basis).*

coated with a finishing agent of unknown composition and consequently have abnormally low resistances, the data for these samples are included in Figure 12 to show that the dependence upon relative humidity of treated materials is similar to that of "clean" samples. The data for the nylon fabric are given for unwashed and once-washed samples, while the yarn values are for an unwashed sample.

Just as with the single fibers studied, the points in Figure 12 for a given material fall on a nearly straight line. Table IX gives the values of n and $[(\log K) - n]$ for the data of Figure 12. These results are consistent with the values tabulated by Hearle [5], although, in view of the wide spread of results reported in Hearle's review, this lack of contradiction does not mean much.

The resistivity of the nylon tire cord is seen to be 20 to 30 times that of the textile monofilaments, and about 3 times that of the 0.023-in. fishing-line nylon. Again, the processing histories are unknown, and it is impossible to ascribe a source for this disagreement. The assumption of a finite surface resistivity does not provide an explanation.

Correlation Between Resistances of Assemblies and Components Thereof

Correlation Between Resistances of Single Fibers and Yarns

As may be concluded from a detailed comparison of Figures 7 and 11, there is no difference within the experimental uncertainty between the volume resistivity of a given material in the form of single fibers and in the form of yarns. In view of the factors that for all of the materials used the staple lengths were several times the sample length, that the surface conductivity is believed to be unimportant, and that the resistance is uniform along the length, it is not surprising that a yarn behaves like a set of similar resistors in parallel. Indeed, even if surface conductivity is important, it would not affect the current distribution in a uniform yarn, since points in different fibers at the same cross section through the yarn would be at the same potential.

Correlation Between Resistances of Yarns and Cloth

The resistance of an acetate fabric was measured in both warp and filling directions, and the resistance of the component yarns was also measured. The fabric was a satin of construction 112 ends/inch by 64 picks/inch, with warp yarns of 75 denier and fill-

TABLE IX. VALUES OF n AND $[(\log K) - n]$ FOR LOGARITHMIC PLOTS OF RESISTIVITY OF FIBER ASSEMBLIES AGAINST MOISTURE CONTENT AT 30°C

Material	n	$(\log K) - n$
Acetate yarn	6.9	9.7
Acetate fabric		
Warp	7.0	9.4
Filling	7.0	9.8
Nylon yarn (oiled)	10.1	5.4
Nylon fabric (not washed)	14.2	3.5
Nylon fabric (washed once)	9.9	6.5
Nylon tire cord	9.6	8.1
Viscose rayon yarn	10.5	8.6
Cuprammonium rayon yarn	11.8	8.8
Cotton yarn	7.9	6.4
Wool yarn	14.5	11.2
Silk yarn	16.8	9.6

TABLE X. RESISTANCES OF 2.0-CM. LENGTHS OF ACETATE FABRIC AND YARNS TAKEN THEREFROM AT 30°C AND 85% R.H.

Sample	Resistance (10^{12} ohms)
Warp yarn—75 denier	44
Filling yarn—300 denier	8.5
Fabric, warp direction—0.5-cm. strip, 22 warp ends	0.65
Fabric, filling direction—0.5-cm. strip, 13 filling yarns	0.65

ing yarns of 300 denier. The resistances of 0.5 cm. × 2 cm. strips of fabric and of 2-cm. lengths of yarn, measured at 85% R.H. and 2000-v. potential difference, are given in Table X. When the resistivities are calculated in the usual way for the yarns—namely, by assuming the cross-sectional area to be equal to the denier divided by 900,000 times the volume density of the material—it is found that the warp ends and filling yarns have approximately the same resistivity.

It is of interest to see how successfully the fabric can be represented as a rectangular grid consisting of relatively small resistances in the filling direction connected by relatively large resistances in the warp direction. So far as the resistance along the filling direction is concerned, there is a set of 13 relatively low resistances in parallel, connected by relatively high resistances at spaces equidistant along their length. Small deviations from uniformity along the filling will result in small inequalities between the potentials at the ends of the warp segments, but these segments have high enough resistance so that the pattern of the current through the filling will be only slightly disturbed. Hence, the resistance in the filling direction should be nearly the resistance of a single filling yarn divided by the number of yarns in the width of the sample measured—that is, 8.5×10^{12} ohms divided by $13 = 0.65 \times 10^{12}$ ohms. This calculated value is the same as the experimental value given in Table X.

So far as the resistance along the warp direction is concerned, there is a set of 22 relatively high resistances in parallel, connected by relatively low resistances at spaces nearly equidistant along their length. Small deviations from uniformity along the warp will result in small inequalities between the potentials at the ends of the filling segments, but in this case these segments have resistances low enough so that the pattern of the current through the warp may be seriously disturbed, and there appear additional current paths which lower the resistance of the sample in the warp direction. The resistance is reduced even further due to the fact that the yarns forming the grid are connected by area-to-area contacts rather than by point-to-point contacts. The overlapping portions of the crosswise yarns present conducting paths parallel to the lengthwise yarns. When the crosswise yarns have high resistance, as in the case of the resistance along the filling direction discussed in the preceding paragraph, the effects of area-to-area contact are small, but when the crosswise yarns have low resistance, the additional current may be substantial and the apparent resistance of the fabric will be decreased. Hence, the resistance in the warp direction could be much lower than the resistance of a single warp end divided by the number of warp ends in the width of the sample measured—that is, 44×10^{12} ohms divided by $22 = 2.0 \times 10^{12}$ ohms. The experimental value given in Table X is indeed only about $\frac{1}{3}$ times as large as this calculated value. The magnitude of this ratio seems reasonable, although it is difficult to give any precise estimate.

It appears, then, that there exists a reasonable basis for predicting the resistance of assemblies in terms of their components, although care must be exercised in the interpretation. This finding will be important in facilitating the study of materials whose resistivities are so high that single-fiber measurements are inordinately difficult.

Summary

1. An apparatus has been constructed to measure the electrical resistance of fibers and fiber assemblies from 10^8 to 10^{16} ohms at specified temperatures and humidities.

2. Results of resistance measurements at 30°C and at relative humidities from 52% to 85% are presented for cotton, wool, silk, hair, casein fiber, nylon, saponified acetate, acetate, viscose rayon, and cuprammonium rayon. These materials were studied in the form of single fibers, yarns, and/or fabrics. The resistivities of Dynel, Orlon, Dacron, Velon, and polyethylene are too high to be studied with the present apparatus, and only lower limits of resistivity at 85% R.H. are given.

3. The resistivities of all materials studied decrease rapidly with increasing moisture content, the resistivities varying inversely as the 7th to 13th power of moisture content.

4. All materials studied were found to be ohmic and largely free from polarization effects at gradients up to several hundred volts/centimeter, the limiting values used in the experiments.

5. From a study of the resistance of nylon filaments varying in diameter from 20 to 200 μ, it was indicated that conduction takes place primarily through the volume of the material, the surface conduction apparently being negligible.

6. Reasonable correlations were found to exist between resistances of fibers and fiber assemblies. Within the experimental uncertainties, the volume resistivity of a given material was found to be the same whether it was in the form of single fibers or yarn. The resistance of a fabric was correlated fairly reasonably with the resistance of its component yarns by considering the fabric to be a rectangular grid of conductors.

Acknowledgment

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An Improved Vibroscope*

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Abstract

An improved model of the constant-frequency type vibroscope† used for measuring single fiber denier is described in detail. This vibroscope has a least count of 0.01 denier, which corresponds roughly to about 0.03 μg. weight in a 1-in. sample. The improvements incorporated into this new model pertain primarily to its speed and ease of use. A description of the important parts is included, and some illustrative data are shown.

IN STUDYING the mechanical properties of textile fibers it is often necessary to measure the relative size or denier of the single filaments. This is a difficult and tedious job because the filaments are so small and weigh so little. A 1-in., 1-denier filament weighs only about 3 μg.; any device designed to weigh this to an accuracy of 1% must be very sensitive. Various techniques have been used in the past for accomplishing this: microscopic study of the cross section, quartz fibers used as a fiber balance for direct weighing, and the vibroscope technique. The latter method affords greater speed and precision than the others, and in recent years has been the most popular. The instrument described herein was developed to make this measurement as rapidly and as easily as possible without sacrificing accuracy.

Theory of the Vibroscope

The vibroscope uses the principle of the "vibrating string," which is fairly well known and which has been used since ancient times. It is the principle which governs the pitch of vibrating stringed instruments such as a piano or a violin, and it is expressed mathematically in equation (1), where f is the frequency of vibration, L is the length of the vibrating section of the string, P is the tension in the string, and m is the linear density of the string or, in the present case, the denier:

$$f = \frac{1}{2L}\sqrt{\frac{P}{m}}. \tag{1}$$

This equation applies to a perfectly flexible string vibrating with small amplitude. If the string is not perfectly flexible and has a stiffness of its own, the relationship is more exactly expressed in equation (2), where R is the radius of fiber and E is its Young's modulus:

$$f = \frac{1}{2L}\sqrt{\frac{P}{m}}\left(1 + \frac{R^2}{L}\sqrt{\frac{\pi E}{P}}\right). \tag{2}$$

By proper design of the instrument, the correction term in equation (2) may be made small (3% or so), and this may be adjusted for in the calibration of the instrument. Since it is m, the linear density or denier, which we wish to measure, we can solve equation (1) for m:

$$m = \frac{P}{4L^2f^2}. \tag{3}$$

It can be seen from equation (3) that an instrument can be designed whereby any two of the three variables on the right-hand side can be held constant, the third being used as the variable to measure m. Gonsalves in his original article* and Montgomery in his recent article† preferred to keep the tension,

* A description of this instrument appeared in the Proceedings of the 75th Anniversary of the Congrès International des Sciences appliquées à l'Industrie Textile (Sept. 1951).

† Dart and Peterson, TEXTILE RESEARCH JOURNAL **19**, 89–93 (1949).

* Gonsalves, V. E., TEXTILE RESEARCH JOURNAL **17**, 369–75 (1947).

† Montgomery, D. J., and Milloway, W. T., TEXTILE RESEARCH JOURNAL **22**, 729–35 (1952).

P, and the length, L, constant, and vary the frequency. This worked quite well, but it gives an inverse square relationship and involves either a nonlinear scale on the instrument or a calculation to be performed before the actual denier is obtained.

In our instrument, we prefer to hold the length and frequency constant, and vary the tension, P. We feel that this has a number of advantages. Perhaps the most important advantage in its operation is that the instrument then can be made direct-reading—that is, the instrument gives directly the denier in a single measurement, without the necessity of secondary measurements or calculations, and requires a minimum of handling of the fibers. The manner and extent of handling is very important in single filament work, especially if the filament is to be used for further tests, as is usually the case. These considerations contribute appreciably to the ease and speed of measurement. Another advantage is that each filament is loaded the same relative amount (about 0.03 g./denier)—that is, the heavier denier has a greater tension and all filaments are treated in the same relative manner. Since the frequency is not a variable, the electronic and sonic systems need not have high fidelity. This, added to the fact that no additional equipment is needed, makes the total cost of the instrument quite reasonable.

Description of the Instrument

The component parts were chosen to combine good precision with ease of use. The audio oscillator is a thousand-cycle electronic audio oscillator. After a warmup period of 15 min. or so, the frequency of the oscillator holds constant to ± 1 cycle/sec. Since the power used is quite small, it has been found that a phonograph pickup crystal is a very satisfactory means of changing the electrical vibration to mechanical vibration; such a crystal is used to drive the top fiber clamp. This crystal is connected to the oscillator through an impedance matching transformer, and gives adequate amplitude without objectionable noise.

A microscope body with rack and pinion coarse adjustment and an inclined monocular eyepiece holder is used for observing the filament. The microscope has a 15 × eyepiece and 6 × objective of 22.7 mm. focal length. A micrometer disc in the eyepiece gives a handy reference point in observing the filament. A small pen-light arrangement is used for illuminating the filament. The maximum illumination is obtained when the light source is shining at right angles to the filament because most filaments are remarkably transparent and the refracted light is easily observed in the microscope.

Various types of dials can be made or found commercially which are quite satisfactory for use on this instrument. One found commercially which is useful and easily available is a precision dial made by National Company—a 4-in. N dial with 100 divisions in 180° and supplied with a vernier. This dial is quite easy to use and also easy to read.

Since the chain is the active measuring element of the instrument, it should be of good linearity and of a noncorroding metal. We have found that either gold or platinum is quite satisfactory. The chain should be of the round-link variety in order that its linear density will not be changed by the manner in which it hangs. The linear density, or weight per unit length, of the chain should be within the range of 20 to 80 mg./cm. Although this is not a hard and fast rule, it seems to give the most satisfactory operation. The linear density of the chain used in our instrument was about 50 mg./cm.

The filament clamps are a very important part of the instrument; these clamps must be extremely light in weight and must grip the filament tightly, but gently enough to cause no damage, since the filament

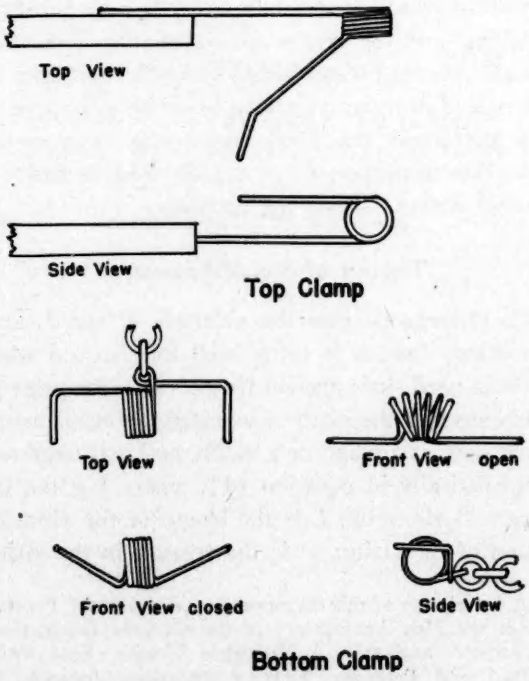

FIG. 1. *Fiber clamp assembly.*

will subsequently be used in other tests. Many types of clamps have been tried, but the most satisfactory one is described here. This clamp is made from fine spring wire wound in a coil spring in such a manner that the coils normally press tightly together. If the coils of this spring are separated and a filament is inserted between them, they will grip the filament when allowed to return to their normal position. This type of clamp has been very satisfactory; our particular version of the clamp is shown in Figure 1. This figure shows the upper and the lower clamps magnified 10 times for clarity. The weight of the bottom clamp is the most critical; we have found that a satisfactory clamp can be made weighing only 5 mg. Five-mil spring stainless-steel wire was used, stainless wire being recommended to prevent weight changes due to corrosion. The general shape of the two clamps is evident from Figure 1. The top clamp wire is soldered to a larger rod, which is then mounted in the needle receptacle of the crystal vibrator. The bottom clamp is made with a small loop, which goes through the first link in the chain. Since these clamps are very small and difficult to handle, a device is used to ease the operation of filament mounting. The bottom clamp was designed to fit into the clamp opening system, which is made from a rebuilt relay with a slot cut in the moving element. However, clamps could easily be designed for opening by hand, the disadvantage being that the manipulation of these small clamps is a rather tedious and delicate job. The filaments are usually handled with cork-lined tweezers.

Since this is a high-precision instrument, it is necessary to mount it on a very rigid mount. The mount shown here is 8-in. channel iron with a ¼-in. plate bolted or welded to one side. This gives a firm mounting free from vibrating elements and free from air currents.

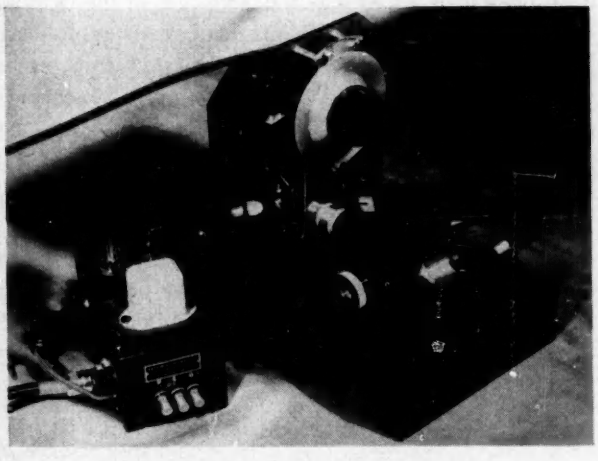

FIG. 2. *Photograph of the vibroscope.*

Figure 2 is a photograph of one of our instruments, showing the arrangement of parts. The vibrating length of the filament is about 1 in. The diameter of the drum on which the chain is wound is calculated from the known constants of the system—*i.e.*, the dial calibration, the exact frequency of the oscillator, the linear density of the chain, and the vibrating length. The exact calibration of the assembled instrument is accomplished by small adjustments in the vibrating length.

Experimental Calibration

Of the number of methods of calibrating the vibroscope a rather successful one substitutes a variable-frequency oscillator for the final fixed one used to drive the upper clamp. The scale readings obtained on a given filament at various frequencies of vibration plotted against the square of the frequency give a straight line, the slope of which is used to calculate the filament denier and to check against the value actually obtained at the fixed frequency of the instrument.

A more direct method of calibration involves a direct weighing of the filament by means of a quartz fiber balance or some other sensitive balance. Without a quartz fiber balance, a comparison between the total denier of a number of filaments and a direct weighing of the bundle serves as an excellent cross-check. For instance, in a series of 24 yarns of 150 denier 41 filaments, direct denier measurements on the 984 filaments in these yarns yielded an average of 3.68 denier per filament. This compares favorably with the calculated value of 3.66. In another series of measurements, 48 different yarns of 75 denier 20 filaments were measured filament by filament to obtain an average. These 960 measurements averaged 3.71 denier, whereas the calculated value is 3.75 denier. The number of filaments to be handled makes this type of measurement a rather tedious one, but it has the advantage of showing up any systematic errors which might occur in the vibroscope calibration.

In another method of checking the accuracy of the vibroscope, the cross-sectional area of the filaments as measured from a photomicrograph is compared with the value obtained from denier measure-

TABLE I

	Denier	
	Vibroscope	Photomicrograph
Yarn 1		
Large filament average	4.21	4.22
Small filament average	2.24	2.23
Yarn 2		
Large filament average	4.91	5.07
Small filament average	3.75	3.73

ments. As an illustration of this method, Table I shows a comparison between the denier as measured by the vibroscope and as calculated from photomicrographs.

These yarns were spun from jets made with two different hole sizes. As a result, the single filament deniers came in two sizes, and the values given are the averages of those within each group. These results show good correlation even though the study involved only 40 filaments.

Some Applications of the Vibroscope

The most obvious application, and the one for which it is most commonly used, is the measurement of single filament denier prior to further testing, such as stress-strain work. This yields relative data on filaments of widely different sizes and allows tests on filament properties at various conditions of stretch or processing. The tests which are commonly made on yarn can also be made on single filaments and the results compared. Also, standard tests can be made on staple filaments which are not obtainable in continuous-filament form.

Although this is the obvious application of the vibroscope, there are a number of other things for which it is very convenient. For instance, it is very useful in studying the uniformity of the filaments under various conditions. Table II gives data for two yarns—one was spun under rather poor uniformity conditions, and the other under good uniformity conditions.

TABLE II. FILAMENT DENIER UNIFORMITIES

				Average deviation	
	Max.	Min.	Ave.	Filament to filament	Along filament
Poor yarn	5.55	1.71	3.77	0.79	0.05
Good yarn	4.25	3.84	4.08	0.08	0.04

In studying the filaments within these yarns, it is possible to determine the kind of filament variation that exists, and, from this, to evaluate other variables within the spinning process. Table II also shows the denier deviations along the length of a given filament, and, in this case, both yarns show rather uniform behavior. If large and small filaments are detected, much can often be learned by studying their stress-strain properties in order to determine the cause of the largeness or smallness. As previously illustrated in the microscopic study, the checking of single filament denier can be of some interest in studying the flow properties of the original spinning dope on being spun through different-size jet holes. The vibroscope, then, may be used as a tool in studying the different mechanisms of flow and, perhaps, viscosities during the spinning operations.

Summary

A detailed description has been presented of an instrument for measuring the denier of a single filament in the range from 0.5 denier to 10.0 denier. This covers the normal useful range of filaments in textile yarns. A brief theoretical discussion has been presented, as well as a description of the details of the construction. This precision instrument has been found to be of great use in the laboratory, and, with proper care and handling, gives excellent performance.

(Manuscript received September 9, 1952.)

The Exact Pattern of a Concentration-Dependent Diffusion in a Semi-infinite Medium, Part II*

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Introduction

In Part I [3] a formal solution of the unidimensional diffusion equation with a variable diffusion coefficient of the form

$$D(C) = D(0)/(1 - \lambda C) \qquad (1)$$

was obtained in a semi-infinite medium (the medium is initially free from diffusing substance and its surface is maintained at a constant concentration throughout the process). When the parameter λ is chosen properly, equation (1) gives a concentration dependence resembling rather closely the types which are often observed in many polymer-solvent systems; however, appropriate experimental examples of D-C data, which are represented quantitatively by the above relationship, are not to be found in the existing literature. Accordingly, from the practical point of view, the formal solution given in Part I is still a matter of only theoretical interest. More recently, it was found that there is another case of $D(C)$ which permits a formal solution of the unidimensional diffusion equation subject to the same initial and boundary conditions as adopted in Part I. It is the $D(C)$ of the form

$$D(C) = D(0)/(1 - \lambda C)^2, \qquad (2)$$

where λ is an arbitrary constant. This form of $D(C)$, when compared with that of equation (1) for the same value of λ, gives a more rapid increase in D with concentration, and is therefore more useful as a mathematical form of the concentration dependence which is encountered in many polymer-solvent systems. In fact, it is shown that equation (2) corresponds quantitatively with the experimental D-C data obtained by Crank and Park [2] for a polystyrene-chloroform system at 25°C. For this reason, the mathematical analysis associated with this diffusion coefficient is of considerable interest from the practical point of view.

The purpose of the present paper is to present a full account of the mathematical solution of this diffusion problem and its connection with the experimental data of Crank and Park [2]. Park [4] refined Crank and Park's original data with a more elaborate procedure; the original results of Crank and Park and the later results of Park are used herein to fit equation (2) to the experimental data.

The Formal Solution

Suppose that a semi-infinite medium of uniform material is exposed to a volume of solvent, and that the solvent is allowed to diffuse into the medium. It is assumed that throughout the process the surface of the medium is maintained at a constant concentration, C_o, and that the medium is initially free from the solvent. Using the same notations as defined in Part I, the diffusion equation to be solved is

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left[\frac{D(0)}{(1 - \lambda C)^2}\frac{\partial C}{\partial x}\right], \qquad (3)$$

and the auxiliary conditions to which the required solution is subject are

$$C(x,0) = 0 \qquad (0 < x < \infty), \qquad (4)$$

$$C(0,t) = C_o \qquad (t > 0). \qquad (5)$$

On introducing the dimensionless variables

$$\frac{C}{C_o} = c, \qquad \frac{x}{2\sqrt{D(0)t}} = \eta, \qquad \lambda C_o = \alpha, \qquad (6)$$

equation (3) reduces to an ordinary differential equation in η of the form

$$\frac{d}{d\eta}\left[\frac{1}{(1 - \alpha c)^2}\frac{dc}{d\eta}\right] = -2\eta\frac{dc}{d\eta}, \qquad (7)$$

and conditions (4) and (5) change, respectively, to

$$c \to 0 \qquad (\eta \to \infty), \qquad (8)$$

$$c = 1 \qquad (\eta = 0). \qquad (9)$$

* Part I appeared in the November, 1952, issue of TEXTILE RESEARCH JOURNAL.

† Associate Professor of Applied Physics.

As in Part I, we are interested only in the case in which the diffusion coefficient increases with increasing concentration, so that it is assumed that $0 < \alpha < 1$.

The substitutions given by

$$\frac{dc}{d\eta} = -\varphi, \tag{10}$$

$$1 - \alpha c = s \tag{11}$$

transform equation (7) to

$$\frac{d}{ds}\left(\frac{\varphi}{s^2}\right) = -\frac{2}{\alpha}\eta. \tag{12}$$

Differentiating both sides of this equation with respect to s, there results

$$\frac{d^2}{ds^2}\left(\frac{\varphi}{s^2}\right) = -\frac{2}{\alpha^2\varphi}, \tag{13}$$

which, on introducing the new variables w and z, defined by

$$w = \frac{\varphi}{s^3}, \qquad z = \frac{1}{s}, \tag{14}$$

reduces to an integrable form:

$$\frac{d^2w}{dz^2} = -\frac{2}{\alpha^2 w}. \tag{15}$$

The first integral of this is given by

$$\frac{dw}{dz} = \pm\left(k - \frac{4}{\alpha^2}\ln w\right)^{\frac{1}{2}}, \tag{16}$$

where k is an integration constant. Combining equations (10), (11), (12), and (14) we have

$$\frac{dw}{dz} = (1 - \alpha c)\left[\frac{2}{\alpha}\eta - \frac{1}{(1 - \alpha c)^3}\frac{dc}{d\eta}\right]. \tag{17}$$

From the condition (8) it follows that $\frac{dc}{d\eta} \to 0$ and $\eta \to \infty$ as $c \to 0$, which, on combining with equations (10), (14), and (17), give the conditions that

$$w \to 0 \text{ and } \frac{dw}{dz} \to \infty \text{ as } c \to 0.$$

These conditions make the elimination of the negative solution in equation (16) possible, and we then have

$$\frac{dw}{dz} = \left(k - \frac{4}{\alpha^2}\ln w\right)^{\frac{1}{2}}. \tag{18}$$

It is easily shown that equation (17) can be rewritten in the form

$$\frac{dw}{dz} = \frac{w}{z} + \frac{2}{\alpha}\frac{\eta}{z},$$

which, by putting $\eta = 0$, gives the condition that

$$\frac{1}{1 - \alpha}\cdot\frac{dw}{dz} = w \text{ at } z = \frac{1}{1 - \alpha}.$$

Inserting this into equation (18) gives an expression for k in the form

$$k = (1 - \alpha)^2\epsilon^2 + \frac{4}{\alpha^2}\ln\epsilon,$$

where ϵ is defined as

$$\epsilon = (w)_{z=\frac{1}{1-\alpha}}. \tag{19}$$

Equation (18) is thus put in the form

$$\frac{dw}{dz} = (1 - \alpha)\epsilon\left(1 - 2\mu\ln\frac{w}{\epsilon}\right)^{\frac{1}{2}}, \tag{20}$$

where μ is a new constant connected with α and ϵ by

$$\mu = \frac{2}{[\epsilon\alpha(1 - \alpha)]^2}. \tag{21}$$

Integrating equation (20) and determining the integration constant therein, using the condition that $w \to 0$ as $z \to 1$, which is derived at once from condition (8), we obtain

$$z = 1 + \frac{1}{1 - \alpha}\int_0^{\frac{w}{\epsilon}}(1 - 2\mu\ln\rho)^{-\frac{1}{2}}\,d\rho.$$

This can be put in a more tractable form as

$$z = 1 + \frac{\sqrt{\pi}\beta}{1 - \alpha}e^{\beta^2}[1 - \text{erf}\,(\beta\theta)], \tag{22}$$

with the introduction of θ and β, defined by

$$\theta = \left(1 - 2\mu\ln\frac{w}{\epsilon}\right)^{\frac{1}{2}}, \tag{23}$$

$$\beta = \frac{1}{2\mu}. \tag{24}$$

Returning back to the original variable c (equation (11)) in terms of z (equation (14)), equation (22) gives

$$c = \frac{f(\theta;\beta)}{\alpha[1 - \alpha + f(\theta;\beta)]}, \tag{25}$$

where, for simplicity's sake, we have put

$$f(\theta;\beta) = \sqrt{\pi}\beta e^{\beta^2}[1 - \text{erf}\,(\beta\theta)]. \tag{26}$$

Following the mathematical deductions given above, it is easily shown that $\theta = 1$ and $\theta \to \infty$ correspond, respectively, to $\eta = 0$ and $\eta \to \infty$. The intermediate variable, θ, involved in equation

(25) varies in the range from 1 to infinity. Since $\eta = 0$, so that $c = 1$, at $\theta = 1$, there obtains from equation (25) the following relation:

$$f(1;\beta) = \alpha, \tag{27}$$

which can be solved to give β in terms of the given parameter α. Since equation (27) is transcendental with respect to β, it is convenient for computational purposes to treat β as a given parameter.

The corresponding expression for η in terms of θ is obtained by combining equations (17), (20), (23) and others, giving

$$\eta = \frac{\beta}{1-\alpha} \times \{[1 - \alpha + f(\theta;\beta)]\theta - \exp[\beta^2(1-\theta^2)]\}. \tag{28}$$

Equations (25) and (28), when β is evaluated in terms of α from equation (27), give the required solution of the problem—that is, the c *vs.* η relation, with θ as an intermediate parameter. These equations consist of tabulated functions only, and hence the procedure of computing the required c *vs.* η plot from them is simple.

It is expected that the solution obtained above with $\alpha \neq 0$ should reduce in the limit when α approaches zero to the well-known solution for a constant diffusion coefficient:

$$c = 1 - \text{erf}\,\eta. \tag{29}$$

This prediction may be verified as follows. In the limit when β approaches zero, $f(1;\beta)$ reduces to the form

$$f(1;\beta) = \sqrt{\pi}\beta[1 + 0(\beta)],$$

which proves that $\beta \to 0$ corresponds to $\alpha \to 0$. When β becomes very small, equation (25) may be expanded in powers of β to give

$$c = 1 - \text{erf}\,(\beta\theta) + 0(\beta). \tag{30}$$

Here, it should be noted that erf $(\beta\theta)$ is not allowed to expand in powers of β since θ may be a large value. Corresponding to equation (30), we obtain from equation (28)

$$\eta = \beta\theta[1 + 0(\beta)]. \tag{31}$$

Eliminating θ from equations (30) and (31) and making $\beta \to 0$ in the resultant equation, it follows that

$$c = 1 - \text{erf}\,\eta,$$

which is the result expected.

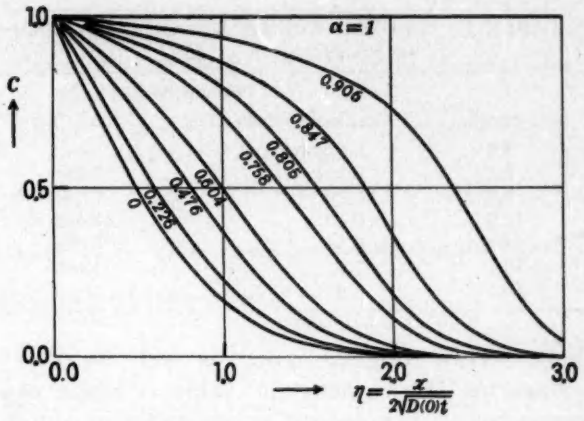

FIG. 1. *The family of concentration-distance curves associated with the diffusion coefficient,* D(C), *given by equation* (*2*).

When β becomes sufficiently large, by applying the asymptotic expression for the complementary error function, equation (27) becomes

$$\alpha = 1 - \frac{1}{2\beta^2} + \frac{3}{4\beta^4} + 0\left(\frac{1}{\beta^6}\right).$$

Hence, the range of α in which we have been interested in the above analysis is known to be covered by the range of β extending from 1 to infinity.

Calculated Concentration-Distance Curves

By taking several values of α in the range $0 < \alpha < 1$, numerical calculations of the formal solution presented above were carried out to obtain the family of concentration-distance curves associated with the diffusion coefficient given by equation (2). The results are shown in Figure 1 in the form of c plotted against η. This provides a typical example of the way in which the diffusion process in one dimension is affected when the diffusion coefficient increases rapidly with concentration in a manner analogous to the exponential relationship.

Experimental Data for a Polystyrene-Chloroform System at 25° C

Crank and Park [2] worked in detail with a polystyrene-chloroform system at 25°C, and demonstrated that in this system the diffusion coefficient depends very strongly upon the concentration of the penetrant. Later, their experimental data were analyzed by Park [4] by means of a more elaborate procedure than that used by Crank and

TABLE I. DIFFUSION COEFFICIENT FOR CHLOROFORM IN POLYSTYRENE AT 25°C

C (% regain)	$D \times 10^{10}$ cm.^{2} sec.$^{-1}$ Crank and Park [2]	Park [4]
5.0	0.024 (extrap.)	—
7.5	0.12	0.085
9.9	0.29	0.186
12.9	0.40	0.503
13.2	0.54	0.560
15.1	1.6	1.60
16.3	6.6	—

Park. Their original data, as well as Park's values for D, are listed in Table I, where concentration, C, is expressed as percentage of equilibrium regain. Park [4] showed that these data, particularly his later values, are fitted satisfactorily by an exponential relationship. It is shown, however, that a similar degree of fit of the data can be obtained with the D-C relationship given by equation (2). In Figure 2, $1/\sqrt{D(C)}$ values computed from the data of Table I are plotted against C; the points are seen to fall approximately on a straight line, thus establishing the applicability of equation (2). From the inclination and the intercept of the straight line, which was drawn to give as good a fit as possible to the plotted points, one can evaluate λ and $D(0)$ corresponding to this experimental case. If λ thus obtained is combined with a given C_o to give the value of α, it is further possible from our formal solution to calculate the concentration-distance curve in the sample corresponding to the given surface concentration. The solid line in Figure 3 represents such a curve calculated for a C_o of 15.1%.

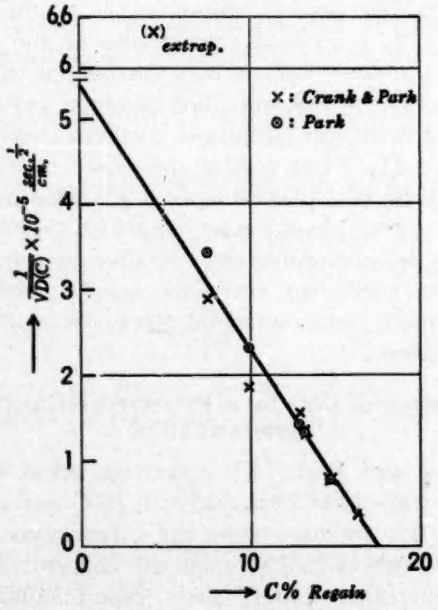

FIG. 2. *Fit of equation (2) to the experimental data for the system polystyrene-chloroform.*

Based on their original D-C data, Crank and Park [2] evaluated the diffusion equation in one dimension by applying the numerical method initiated by Crank and Henry [1], and obtained the concentration-distance curve at the time when the sample sheet maintained at 15.1% surface concentration had reached half the equilibrium sorption. Their calculated curve is represented in the form of C plotted against x divided by the thickness of sheet, l. It is, however, possible to transform their curve into the c *vs.* η plot by use of the identity

$$\eta = \frac{x}{l} \Big/ \sqrt{D(0)\,\frac{t}{l^2}},$$

if t/l^2 at the time of half sorption and $D(0)$ are known. This transformation is permissible only when the sheet is still behaving as a semi-infinite medium, even at the time of half sorption. That this was true in the present case is observed from Crank and Park's calculated curve (see [2]). The t/l^2 and $D(0)$ values in question are given in Crank and Park's paper; it should be noted that the $D(0)$ value indicated therein is only an approximate one which was determined by extrapolation from $D(C)$'s obtained at concentrations greater than 7.5% regain. The c *vs.* η curve obtained in such a way is shown in Figure 3. The two curves plotted are similar in essential features, but differ quantitatively to some extent

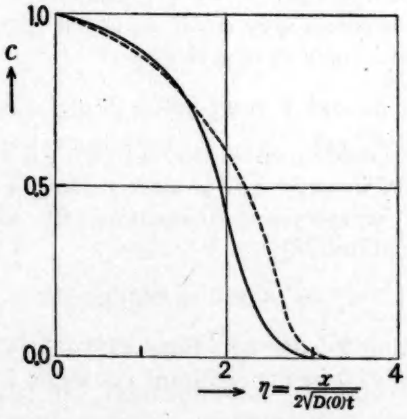

FIG. 3. *Comparison of calculated concentration-distance curves: ----, Crank and Park (numerical); ——, Fujita (formal).*

relative to one another. This numerical difference may be attributed mainly to the marked difference in $D(0)$ values used in both calculations; the $D(0)$ value used by Crank and Park was 0.024×10^{-10} cm.^{2}/sec., whereas the author's $D(0)$ was 0.0356×10^{-10} cm.^{2}/sec. Such a difference in the $D(0)$ values caused the $D(C)/D(0)$ plot in Crank and Park's calculation to shift about 1.5 times above that in the author's calculation, and thus resulted in the discrepancy shown in Figure 3.

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2. Crank, J., and Park, G. S., *Trans. Faraday Soc.* **45**, 240–9 (1949).
3. Fujita, H., TEXTILE RESEARCH JOURNAL **22**, 757–60 (1952).
4. Park, G. S., *Trans. Faraday Soc.* **46**, 684–97 (1950).

(*Manuscript received October 20, 1952.*)

Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

"Mechanics of Elastic Performance of Textile Materials"

Supplement to Part IX*

FABRIC RESEARCH LABORATORIES, INC.
Boston, Massachusetts
October 29, 1952

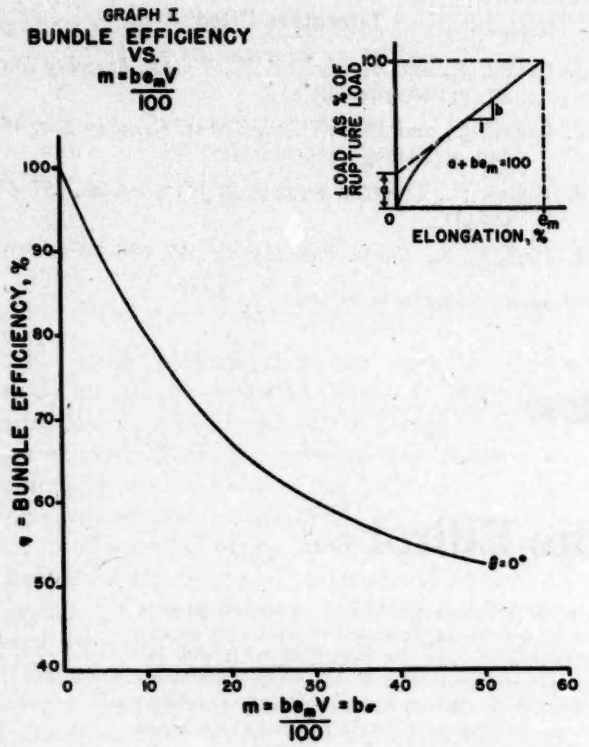
To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

In Part IX the writers presented an analysis of the factors affecting the translation of fiber tensile strength into yarn strength. The method of approach which was used involved the expression of the theoretical results in terms of a great many parameters. It will be shown in this note that the large number of influencing parameters may be reduced to a single one, thereby simplifying theoretical and practical calculations, but at the expense of direct physical visualization of the mechanisms.

Part of the analysis in the above-mentioned article involved the solution of fiber bundles, which solution was shown to be the limiting case of yarn with twist approaching zero. For the sake of consistency and clarity, a similar approach was used for both bundles and yarns, and, consequently, the results for both cases were presented as functions of the same parameters. These parameters are: e_m, the mean elongation to break of the fibers (%); v, the coefficient of variation of fiber elongation to break; a/b, the ratio of load intercept to slope of the linear approximation to the fiber stress-strain curve near rupture (see Graph I); and θ, the yarn surface helix angle (0 for the bundle). Various families of curves of efficiency *versus* e_m for

* Part IX, entitled "Factors Affecting the Translation of Certain Mechanical Properties of Cordage Fibers into Cordage Yarns," by M. M. Platt, W. G. Klein, and W. J. Hamburger, appeared in the October, 1952, issue of TEXTILE RESEARCH JOURNAL, pp. 641–67.



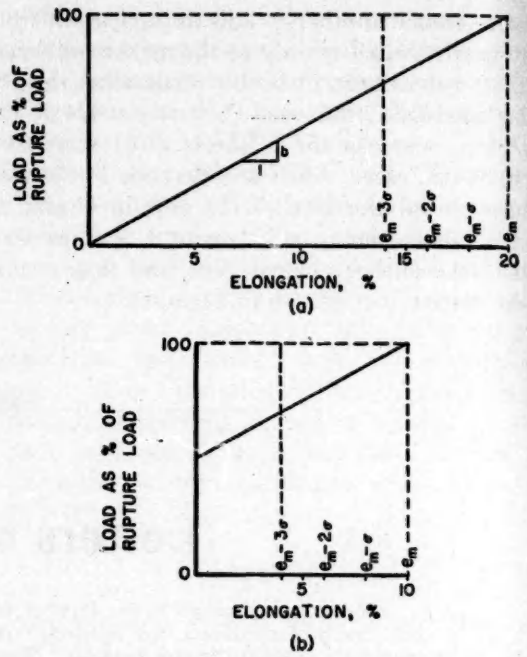


FIG. 1.

bundles and *versus* θ for twisted yarns have been determined for a wide range of the other variables.

While these curves cover all cases, it is possible to define a *single* parameter which will nearly always be an index of translational efficiency, and which in the case of a parallel bundle will be uniquely related to this efficiency. This parameter, m, is the slope of the load-elongation curve near rupture (the parameter b above) in terms of rate of rise per standard deviation of extension to break. Thus, if the load rises the amount be_m in an extension e_m, it rises $be_m \times \left(\frac{\sigma}{e_m}\right)$ or $b\sigma$ in an extension σ. We shall call the product $b\sigma$ the parameter m.

To see that m is really a translation index, consider first the case of a bundle of parallel fibers. In Figure 1(a) is shown the load-elongation approximation for a fiber population with mean breaking elongation 20% and standard deviation 2%. In Figure 1(b) is shown a population derived from Figure 1(a) by shifting the zero axis 10 units to the right so that here the mean elongation is 10%. In terms of previous work the two population parameters are as follows: for 1(a), $e_m = 20\%$, $v = 10\%$, $a/b = 0$; for 1(b), $e_m = 10\%$, $v = 20\%$, $a/b = 10$. In each case, however, $b = 5$ and $\sigma = 2$, so that both m's are 10. It is easy to see that the fibers have no "memory" of their condition before reaching the region inside the dotted lines, and, since the two cases are indistinguishable within this region, they will translate to the same degree.

Similarly, it can be seen that if there be performed a simple multiplication transform on the elongation axis (*e.g.*, let $e' = 2e$, then $\sigma' = 2\sigma$), e_m, b, a/b, and σ will in general all change, but the product $b\sigma$ $\left(\frac{b\ e_m\ v}{100}\right)$ will remain constant, as will the position of the load-elongation curve relative to the breaking distribution curve (determined by σ).

Graph I shows efficiency of translation of fibers into bundles *versus* m. Unfortunately, this unique correspondence between translational efficiency and m exists only for the untwisted case, but, except for extreme cases of high twist and large changes in e_m, a lower value of m indicates a better translational efficiency into any structure.

The results given by the sets of curves mentioned above have been shown to agree very well with experimental work until reaching high helix angles. Here the experimental results are consistently slightly lower than those predicted. A plausible explanation for this is that one of the factors neglected in the theoretical development is no longer negligible at high twists—namely, variation of twist and its ef-

fects. It will be recalled, first, that the length of yarn over which rupture occurs is quite small and, second, that the yarn strength becomes quite sensitive to variations in the helix angle when the angle is high. It is easy to visualize a yarn twist over a short length significantly in excess of the average twist, due largely perhaps to yarn cross-section and processing irregularities. Since the test length is considerably larger than the "rupture length," there is no question of averaging weak and strong sections. The result instead would simply be to lower the average of a large number of breaks, which indicates that there should be a length dependence of breaking strength. This has not been demonstrated, but, in view of the number and magnitude of the variables involved and the small differences to be explained, no statistically significant result could be expected without a very large number of carefully controlled tests, and the expenditure of an unjustifiable amount of time. There would also be great difficulty in experimentally ascertaining twist/unit length variations over short lengths of the cordage yarns studied.

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W. G. KLEIN
W. J. HAMBURGER

Correction

In the article "Mechanics of Elastic Performance of Textile Materials: Part X: Some Aspects of Elastic Behavior at Low Strains," by Walter J. Hamburger, Milton M. Platt, and Henry M. Morgan, which appeared in the November, 1952, issue of TEXTILE RESEARCH JOURNAL, errors appeared on the following pages:

p. 697: The right-hand expression in equation (1) should read $\frac{1}{1 + \frac{d_i}{d_o}}$ instead of $\frac{\frac{1}{d_i}}{1 + d_o}$.

p. 703: The symbol on line 8 of the left-hand column should be θ_e instead of ρ_e.

p. 714: Equation (14) should read $\alpha = 180 - 360 \frac{Le}{\pi d}$.

p. 716: The first equation under the bottom drawing in Figure 21 should read $A = \pi ab = \pi r^2$.

p. 719: On line 10 of the left-hand column "Figure 5" should read "Figure 23."

p. 720: Equation (20) should read:

$$\frac{1}{\rho_{cr}} = \frac{1 + C/B}{2r_o} \pm \sqrt{\left(\frac{1 - C/B}{2r_o}\right)^2 + \frac{\pi^2 C/B}{L^2}}.$$

Textile Research Journal

Volume XXII, Numbers 1–12 (January–December), 1952

Month	*Number*	*Pages*	*Month*	*Number*	*Pages*
January	1	1–74	July	7	441–502
February	2	75–152	August	8	503–560
March	3	153–222	September	9	561–622
April	4	223–292	October	10	623–694
May	5	293–378	November	11	695–764
June	6	379–440	December	12	765–834

Author and Title Index

	No.	Page
Alder, Marilyn G. (with Eyring, Rossmassler, Christensen). Forced Vibrations of Polyamide Monofils	4	223
Alexander, E. Optimal Twist in Staple Yarn	8	503
Algera, L. The Visibility of the "Cuticula" of Wool Under the Phase-Contrast Microscope (Letter to the Editor)	2	97
Appel, William D. (with Bogaty, Campbell) Some Observations on the Evaporation of Water from Cellulose	2	75
The Oxidation of Cellulose by Ozone in Small Concentrations	2	81
Araki, Tsunao. Studies on Cellulose Acetate: Part III: Combination of Sulfuric Acid During the Acetylation of Cellulose and the Mechanism of Acetylation	10	630
Arthur, Harry E. (with Marth, Berkley). Fiber Fineness (Micronaire), Neps in Card Web, and Yarn Appearance Grades	9	561
Backer, Stanley Cover Factor Adjustments for Twill Weaves (Letter to the Editor)	6	435
The Mechanics of Bent Yarns	10	668
Balmer, Clifford E. (with Hasselstrom, Coles, Hannigan, Keeler, Brown). The Behavior of Nylon Oxford Cloth "41" on Pyrolysis	11	742
Balog, John Adolph (with Mack, Jordan). A Comparative Study of Sonic and Mechanical Home Washers: Part I: Strength and Dimensional Changes	1	30
Bauer, Frederick W. (with Pacsu) Cellulose Studies		
Part XVII: The Heterogeneous Acid Degradation of Cellulose	6	385
Part XVIII: The Homogeneous Degradation of Cellulose in Phosphoric Acid	6	397
Bayley, C. H. (with Weatherburn). The Sorption of Synthetic Surface-Active Compounds by Textile Fibers	12	797
Beard, R. L. (with Dyer, Faw). Some of the Factors Influencing Yarn Tension in Warping	7	487
Berkley, Earl E. (with Marth, Arthur). Fiber Fineness (Micronaire), Neps in Card Web, and Yarn Appearance Grades	9	561
Blum, Robert (with Stahl). Enzymic Degradation of Cellulose Fibers	3	178
Bogaty, Herman (with Campbell, Appel) Some Observations on the Evaporation of Water from Cellulose	2	75
The Oxidation of Cellulose by Ozone in Small Concentrations	2	81
Breazeale, F. B. (with Irvin). An Automatic Yarn Load-Elongation Recorder	8	549
Brown, Robert J. (with Hasselstrom, Coles, Balmer, Hannigan, Keeler). The Behavior of Nylon Oxford Cloth "41" on Pyrolysis	11	742
Bryant, F. Determination of the Fat Content of Silk Soaking Emulsions (Letter to the Editor)	6	433
Chromatographic Studies of the Silk Fiber		
Part I: The Amino Acid Composition of Two Sericin Fractions	8	523
Part II: Fractionation of a Fibroin Hydrolyzate	8	525
The Ferroxyl Reagent Applied to a Study of Knitting Needle Corrosion (Letter to the Editor)	8	553
Buck, George S., Jr. An Analysis of the Consumer Quality Characteristics of Cotton: Implications for Research (T.R.I. Annual Meeting, 1951)	2	117
Budd, C. B. Author's Comments on a Letter to the Editor by Hermanne, Quintelier ("A Fatigue Test for Tire Cords," by C. B. Budd)	2	97
Campbell, Kenneth S. Some Observations on the Evaporation of Water from Cellulose (with Bogaty, Appel)	2	75
The Oxidation of Cellulose by Ozone in Small Concentrations (with Bogaty, Appel)	2	81
Relation Between Certain Defects in Dyed Fabrics and Mechanical Damage in Wet Processing (with Cates, Rutherford)	10	623
Cates, D. M. (with Campbell, Rutherford). Relation Between Certain Defects in Dyed Fabrics and Mechanical Damage in Wet Processing	10	623
Chen, Mei Chio (with Ree, Eyring). Stress Relaxation and Shrinkage in Fibers	6	416
Christensen, Carl J. (with Eyring, Alder, Rossmassler). Forced Vibrations of Polyamide Monofils	4	223
Coles, Harold W. (with Hasselstrom, Balmer, Hannigan, Keeler, Brown). The Behavior of Nylon Oxford Cloth "41" on Pyrolysis	11	742
Condo, Fred E. (with King, Weil, Rutherford). The Evaluation of Textile Sizes	9	567
Corley, J. R. (with Simpson, Landstreet). An Evaluation of Long- and Short-Term Variation in Sliver and Roving	1	42
Cucullu, Alva F. (with Honold, Poynot). Heat-Resistance of Partially Acetylated Cotton Fabrics	1	25
Correction	3	222
Dart, S. Leonard (with Peterson). An Improved Vibroscope	12	819
Daul, George C. (with Reinhardt, Reid). Studies on the Partial Carboxymethylation of Cotton	12	787
Crease-Resistant Cloth from Partially Carboxymethylated Cotton	12	792
Davis, S. Jack. A Method of Repetitive Longitudinal Sectioning of Cords and Fabrics for Microscopic Examination	3	192
Dean, J. D. (with Fleming, O'Connor). Effects of Unfiltered Carbon Arc Light in Accelerated Weathering of Cotton and Other Textiles	9	609
de Vries, H. Double Refraction Measurement of Fibers (Letter to the Editor)	9	619
Dyer, R. F. (with Faw, Beard). Some of the Factors Influencing Yarn Tension in Warping	7	487
Earland, Christopher (with Johnson). The Treatment of Wool with Sodium Chlorite	9	591
Elliott, A. The α-β Transformation in Stretched Hair	12	783
Eyring, Henry Forced Vibrations of Polyamide Monofils (with Alder, Rossmassler, Christensen)	4	223
Stress Relaxation and Shrinkage in Fibers (with Chen, Ree)	6	416
Faw, W. G. (with Dyer, Beard). Some of the Factors Influencing Yarn Tension in Warping	7	487
Fisher, D. C. (with Roberts). Analysis of Staple Fiber Mixtures	8	509
Fleming, C. M. (with Dean, O'Connor). Effects of Unfiltered Carbon Arc Light in Accelerated Weathering of Cotton and Other Textiles	9	609
Fletcher, Hazel M. (with Roberts) The Geometry of Plain and Rib Knit Cotton Fabrics and Its Relation to Shrinkage in Laundering	2	84
The Geometry of Knit Fabrics Made of Staple Rayon and Nylon and Its Relationship to Shrinkage in Laundering	7	446
Fox, Kenneth R. Technical Problems of the Textile Industry (T.R.I. Annual Meeting, 1951)	1	60

	No.	Page
Frederick, E. B. Development of a Sewability Test for Cotton Fabrics	10	687
Frick, J. G., Jr. (with Schuyten, Weaver, Reid). Formation of Cellulose Ethers in Water-Repellency Treatment of Cotton with Stearamidomethylpyridinium Chloride	6	424
Fujita, Hiroshi		
A Method of Determining the Concentration Dependence of the Diffusion Coefficient (Letter to the Editor) (with Kishimoto)	2	94
A Numerical Solution of the Differential Equation for Adsorption-Controlled Diffusion in a Solid	4	281
Correction (Letter to the Editor)	8	556
The Exact Pattern of a Concentration-Dependent Diffusion in a Semi-infinite Medium		
Part I	11	757
Part II	12	823
Glim a n, Henry (with Sunthankar). Silicon-Containing Azo Dyes: Part III: Dyeing Properties, Absorption Spectra, and pH Range	9	574
Gluffria, Ruth (with Tripp). Effects of Tension on the Swelling of Cotton Fibers	1	21
Goldthwait, Charles F. (with Murphy, Lohmann, Smith). Mercerization of Yarn—Experimental Apparatus and Techniques	8	540
Grant, James N.		
Influence of Cross-Sectional Shape of Raw Cotton on Dimensional Changes in Mercerization Without Tension (with Orr, Humphreys)	2	89
Effects of Mechanical Processing of Cotton on the Physical Properties of Fibers (with Morlier, Scott)	10	682
Grimes, Mary Anna. Cotton Defoliation and Fiber Maturity	10	637
Hamalainen, Carl (with Warren, Reid). Action of Cyanuric Chloride on Cotton Cellulose	9	584
Hamburger, Walter J.		
Mechanics of Elastic Performance of Textile Materials		
Part IX: Factors Affecting the Translation of Certain Mechanical Properties of Cordage Fibers into Cordage Yarns (with Platt, Klein)	10	641
Supplement to Part IX (Letter to the Editor)	12	827
Part X: Some Aspects of Elastic Behavior at Low Strains (with Platt, Morgan)	11	695
Correction	12	829
Hannigan, Mary (with Hasselstrom, Coles, Balmer, Keeler, Brown). The Behavior of Nylon Oxford Cloth "41" on Pyrolysis	11	742
Hasselstrom, Torsten (with Coles, Balmer, Hannigan, Keeler, Brown). The Behavior of Nylon Oxford Cloth "41" on Pyrolysis	11	742
Hermanne, L. (with Quintelier). Fatigue of Tire Cords as a Function of Twist (Letter to the Editor)	2	95
Hersh, S. P. (with Montgomery). Electrical Resistance Measurements on Fibers and Fiber Assemblies	12	805
Heyn, A. N. J. Observations of the Birefringence and Refractive Index of Synthetic Fibers with Special Reference to Their Identification	8	513
Higgins, S. P., Jr. (with McKnight). Practical Application of Servomechanism Techniques to a Process-Control Problem	3	203
Hoerner, S. F. Aerodynamic Properties of Screens and Fabrics	4	274
Hoffman, R. M. Some Theoretical Aspects of Yarn and Fabric Density	3	170
Hoffpauir, Carroll L. (with Pons). Colorimetric Determination of the pH of Cotton Fiber	3	200
Honold, Edith (with Poynot, Cucullu). Heat-Resistance of Partially Acetylated Cotton Fabrics	1	25
Correction	3	222
Hopper, Turner H. Check Sample Testing of Physical Properties of Cotton with Instruments	7	472
Humphreys, Geraldine C. (with Orr, Grant). Influence of Cross-Sectional Shape of Raw Cotton on Dimensional Changes in Mercerization Without Tension	2	89
Irvin, H. D. (with Breazeale). An Automatic Yarn Load-Elongation Recorder	8	549
Jameson, Lake Hugh (with Whittier, Schiefer). Factors Affecting the Properties of Rayon Fabrics	9	599
Johnson, Kenneth G. (with Earland). The Treatment of Wool with Sodium Chlorite	9	591
Jordan, Mildred Naomi (with Mack, Balog). A Comparative Study of Sonic and Mechanical Home Washers: Part I: Strength and Dimensional Changes	1	30
Keeler, Margaret M. (with Hasselstrom, Coles, Balmer, Hannigan, Brown). The Behavior of Nylon Oxford Cloth "41" on Pyrolysis	11	742
King, David E. (with Weil, Condo, Rutherford). The Evaluation of Textile Sizes	9	567
Kishimoto, Akira (with Fujita). A Method of Determining the Concentration Dependence of the Diffusion Coefficient (Letter to the Editor)	2	94
Klein, W. G. (with Platt, Hamburger). Mechanics of Elastic Performance of Textile Materials: Part IX: Factors Affecting the Translation of Certain Mechanical Properties of Cordage Fibers into Cordage Yarns	10	641
Supplement to Part IX (Letter to the Editor)	12	827
Kratz, Robert F. (with Stam, White). The Swelling of Human Hair in Water and Water Vapor	7	448
Kubu, E. T.		
The Stress Relaxation of Fibrous Materials		
I. Instrumentation and Preliminary Results	12	767
II. Kinetics of the Reduction of Wool Keratin by Cysteine (with Montgomery)	12	778
Lake, G. K. Properties of Fabrics Made from Several Synthetic Fibers and Their Impact on the Textile Industry (T.R.I. Annual Meeting, 1951)	2	138
Landstreet, C. B. (with Simpson, Corley). An Evaluation of Long- and Short-Term Variation in Sliver and Roving	1	42
Langston, James H. Sizing of Spun Nylon Yarns with Various Agents	2	111
Lindsley, Charles H. The Use of Density Gradient Columns for the Determination of Specific Gravity (Letter to the Editor)	4	287
Loeb, Leopold (with Welo, Ziifle). Swelling Capacities of Fibers in Water: Part I: Desiccation Rate Measurements	4	254
Lohmann, Idas W. (with Goldthwait, Murphy, Smith). Mercerization of Yarn—Experimental Apparatus and Techniques	8	540
Mack, Pauline Beery (with Balog, Jordan). A Comparative Study of Sonic and Mechanical Home Washers: Part I: Strength and Dimensional Changes	1	30
Magne, Frank C. (with Skau). Nonfreezing Water and Nonfreezing Benzene Capacities of Cottons and Modified Cottons	11	748
Marth, Charles T. (with Arthur, Berkley). Fiber Fineness (Micronaire), Neps in Card Web, and Yarn Appearance Grades	9	561
Mazumdar, A. K. (with Sarkar, Pal). The Nature of the Hemicelluloses of Jute Fiber: Part I	8	529
McDonald, Allan W. (with Welo, Ziifle). Swelling Capacities of Fibers in Water: Part II: Centrifuge Studies	4	261
McKnight, G. W. (with Higgins). Practical Application of Servomechanism Techniques to a Process-Control Problem	3	203
Mercer, E. H. The Supercontraction of Keratin	7	476
Milloway, W. T. (with Montgomery). The Vibroscopic Method for Determination of Fiber Cross-Sectional Area	11	729
Montgomery, D. J.		
The Vibroscopic Method for Determination of Fiber Cross-Sectional Area (with Milloway)	11	729
The Stress Relaxation of Fibrous Materials: II. Kinetics of the Reduction of Wool Keratin by Cysteine (with Kubu)	12	778
Electrical Resistance Measurements on Fibers and Fiber Assemblies (with Hersh)	12	805
Morehead, Frederick F.		
The High-Contrast (Wide-Field) Electron Microscope Objective and Fiber Replicas	6	379
A Method for Studying the Effect of Humidity on the Cross-Sectional Swelling of Some Common Fibers	8	535
Morgan, Henry M. (with Hamburger, Platt). Mechanics of Elastic Performance of Textile Materials: Part X: Some Aspects of Elastic Behavior at Low Strains	11	695
Correction	12	829
Morlier, Ora W. (with Grant, Scott). Effects of Mechanical Processing of Cotton on the Physical Properties of Fibers	10	682
Murphy, Alton L. (with Goldthwait, Lohmann, Smith). Mercerization of Yarn—Experimental Apparatus and Techniques	8	540
Newton, Russell B. Research Pays Off (T.R.I. Annual Meeting, 1951)	1	65
Nickerson, R. F. "The Reaction of Cellulose with Formaldehyde," by Wagner and Pacsu (Letter to the Editor)	8	554
Nistico, F. (with Sprague, Work). A High-Speed Recording Yarn Tensiometer	2	99
Nuessle, A. C. (with Wolfrom). Some Observations on the Wetting of Greige Cotton	4	246
O'Connor, R. T. (with Dean, Fleming). Effects of Unfiltered Carbon Arc Light in Accelerated Weathering of Cotton and Other Textiles	9	609
O'Reilly, D. F. (with Whitwell, Steele, Wakelin). Properties of Apparel Wools: II. Modification of Fiber Surface During Worsted Processing	7	441
Orr, Rollin S. (with Humphreys, Grant). Influence of Cross-Sectional Shape of Raw Cotton on Dimensional Changes in Mercerization Without Tension	2	89
Pacsu, Eugene		
Cellulose Studies		
Part XVI: The Reaction of Cellulose with Formaldehyde (with Wagner)	1	12
Part XVII: The Heterogeneous Acid Degradation of Cellulose (with Bauer)	6	385
Part XVIII: The Homogeneous Degradation of Cellulose in Phosphoric Acid (with Bauer)	6	397
Painter, E. V.		
Mechanics of Elastic Performance of Textile Materials: Part VIII: Graphical Analysis of Fabric Geometry	3	153
Correction	8	557
Locating a Fabric on the Fabric Geometry Graph (Letter to the Editor)	8	556
Pal, K. B. (with Sarkar, Mazumdar). The Nature of the Hemicelluloses of Jute Fiber: Part I	8	529
Peterson, L. E. (with Dart). An Improved Vibroscope	12	819

	No.	Page
Platt, Milton M. Mechanics of Elastic Performance of Textile Materials		
Part IX: Factors Affecting the Translation of Certain Mechanical Properties of Cordage Fibers into Cordage Yarns (with Klein, Hamburger)	10	641
Supplement to Part IX (Letter to the Editor)	12	827
Part X: Some Aspects of Elastic Behavior at Low Strains (with Hamburger, Morgan)	11	695
Correction	12	829
Pons, Walter A., Jr. (with Hoffpauir). Colorimetric Determination of the pH of Cotton Fiber	3	200
Poynot, Janice M. (with Honold, Cucullu). Heat-Resistance of Partially Acetylated Cotton Fabrics	1	25
Correction	3	222
Quintelier, G. (with Hermanne). Fatigue of Tire Cords as a Function of Twist (Letter to the Editor)	2	95
Ray, L. G., Jr. The Role of Synthetic Fibers in the Textile Industry of the Future (T.R.I. Annual Meeting, 1951)	2	144
Ree, Taikyue (with Chen, Eyring). Stress Relaxation and Shrinkage in Fibers	6	416
Regnery, Walter. Blending of Cotton by Fineness Determination and Other Applications of Research in Mill Operation (T.R.I. Annual Meeting, 1951)	1	49
Reid, J. David Formation of Cellulose Ethers in Water-Repellency Treatment of Cotton with Stearamidomethylpyridinium Chloride (with Schuyten, Weaver, Frick)	6	424
Action of Cyanuric Chloride on Cotton Cellulose (with Warren, Hamalainen)	9	584
Studies on the Partial Carboxymethylation of Cotton (with Daul, Reinhardt)	12	787
Crease-Resistant Cloth from Partially Carboxymethylated Cotton (with Daul, Reinhardt)	12	792
Reinhardt, Robert M. (with Daul, Reid) Studies on the Partial Carboxymethylation of Cotton	12	787
Crease-Resistant Cloth from Partially Carboxymethylated Cotton	12	792
Roberts, E. D. (with Fisher). Analysis of Staple Fiber Mixtures	8	509
Roberts, S. Helen (with Fletcher) The Geometry of Plain and Rib Knit Cotton Fabrics and Its Relation to Shrinkage in Laundering	2	84
The Geometry of Knit Fabrics Made of Staple Rayon and Nylon and Its Relationship to Shrinkage in Laundering	7	446
Rossmassler, Stephen A. (with Eyring, Alder, Christensen). Forced Vibrations of Polyamide Monofils	4	223
Rutherford, Henry A. The Evaluation of Textile Sizes (with King, Weil, Condo)	9	567
Relation Between Certain Defects in Dyed Fabrics and Mechanical Damage in Wet Processing (with Cates, Campbell)	10	623
Sarkar, P. B. (with Mazumdar, Pal). The Nature of the Hemicelluloses of Jute Fiber: Part I	8	529
Schiefer, Herbert F. Interpretation of Tests for Resistance to Abrasion of Textiles (with Werntz)	1	1
Factors Affecting the Properties of Rayon Fabrics (with Jameson, Whittier)	9	599
Schuyten, H. A. (with Weaver, Frick, Reid). Formation of Cellulose Ethers in Water-Repellency Treatment of Cotton with Stearamidomethylpyridinium Chloride	6	424
Scott, John M. (with Grant, Morlier). Effects of Mechanical Processing of Cotton on the Physical Properties of Fibers	10	682
Segall, G. H. A Theory of Water-Resistant Fabrics	11	736
Simpson, J. (with Landstreet, Corley). An Evaluation of Long- and Short-Term Variation in Sliver and Roving	1	42
Skau, Evald L. (with Magne). Nonfreezing Water and Nonfreezing Benzene Capacities of Cottons and Modified Cottons	11	748
Smith, Herbert O. (with Goldthwait, Murphy, Lohmann). Mercerization of Yarn—Experimental Apparatus and Techniques	8	540
Sprague, B. S. (with Nistico, Work). A High-Speed Recording Yarn Tensiometer	2	99
Spurlin, H. M. The Homogeneous Degradation of Cellulose (Letter to the Editor)	10	693
Stahl, William H. (with Blum). Enzymic Degradation of Cellulose Fibers	3	178
Stam, Paul B. (with Kratz, White). The Swelling of Human Hair in Water and Water Vapor	7	448
Steele, R. O. (with O'Reilly, Whitwell, Wakelin). Properties of Apparel Wools: II. Modification of Fiber Surface During Worsted Processing	7	441
Sunthankar, S. V. (with Gilman). Silicon-Containing Azo Dyes: Part III: Dyeing Properties, Absorption Spectra, and pH Range	9	574
Tallant, John D. Use of a Servo System for Automatic Operation of the Fibrograph	9	617
Textile Research Institute Staff. Review of Textile Research and Development During 1951	5	293
Tripp, Verne W. (with Giuffria). Effects of Tension on the Swelling of Cotton Fibers	1	21
Valko, Emery I. The Principles of Textile Finishing	3	213
von Bergen, Werner (with Wakelin). Properties of Apparel Wools: I. Preliminary Report on Worsted Processing Trials (T.R.I. Annual Meeting, 1951)	2	123
Wagner, Robert E. (with Pacsu). Cellulose Studies: Part XVI: The Reaction of Cellulose with Formaldehyde	1	12
Wakelin, James H. Properties of Apparel Wools I. Preliminary Report on Worsted Processing Trials (with von Bergen) (T.R.I. Annual Meeting, 1951)	2	123
II. Modification of Fiber Surface During Worsted Processing (with O'Reilly, Whitwell, Steele)	7	441
Ward, Wilfred H. The Molecular Size of Proteins from Several Wools Solubilized in Aqueous Urea	6	405
Wardrop, A. B. The Low-Angle Scattering of X-Rays by Conifer Tracheids (Letter to the Editor)	4	288
Warren, Jane (with Reid, Hamalainen). Action of Cyanuric Chloride on Cotton Cellulose	9	584
Waterman, Alan T. Building Our National Scientific Capital to Yield Applied Research Interest for Industry in the Future (T.R.I. Annual Meeting, 1951)	1	69
Weatherburn, A. S. (with Bayley). The Sorption of Synthetic Surface-Active Compounds by Textile Fibers	12	797
Weaver, J. W. (with Schuyten, Frick, Reid). Formation of Cellulose Ethers in Water-Repellency Treatment of Cotton with Stearamidomethylpyridinium Chloride	6	424
Weil, Henry A. (with King, Condo, Rutherford). The Evaluation of Textile Sizes	9	567
Wells, Richard D. Position of the Textile Industry in Relation to Research and Development (T.R.I. Annual Meeting, 1951)	1	53
Welo, Lars A. Swelling Capacities of Fibers in Water Part I: Desiccation Rate Measurements (with Ziifle, Loeb)	4	254
Part II: Centrifuge Studies (with Ziifle, McDonald)	4	261
Werntz, Carl W. (with Schiefer). Interpretation of Tests for Resistance to Abrasion of Textiles	1	1
White, Howard J., Jr. (with Stam, Kratz). The Swelling of Human Hair in Water and Water Vapor	7	448
Whittier, Benjamin L. (with Jameson, Schiefer). Factors Affecting the Properties of Rayon Fabrics	9	599
Whitwell, J. C. (with O'Reilly, Steele, Wakelin). Properties of Apparel Wools: II. Modification of Fiber Surface During Worsted Processing	7	441
Wolfrom, R. E. (with Nuessle). Some Observations on the Wetting of Greige Cotton	4	246
Work, R. W. (with Nistico, Sprague). A High-Speed Recording Yarn Tensiometer	2	99
Wrotnowski, Arthur C. Some Properties of Thermoplastic Fiber-Bonded Fabrics	7	480
Ziffle, Hilda M. Swelling Capacities of Fibers in Water Part I: Desiccation Rate Measurements (with Welo, Loeb)	4	254
Part II: Centrifuge Studies (with Welo, McDonald)	4	261

Subject Index

	No.	Page
Abrasion-Resistance: *See* **Abrasion of Textiles**		
Abrasion of Textiles, Interpretation of Tests for Resistance to (Schiefer, Werntz)	1	1
Absorption Spectra: *See* **Azo Dyes**		
Acetylated Cotton: *See* **Cotton Fabrics**		
Acetylation: *See* **Cellulose Acetate**		
Aerodynamic Properties: *See* **Screens and Fabrics**		
Amino Acids: *See* **Silk Fiber**		
Azo Dyes, Silicon-Containing: Part III: Dyeing Properties, Absorption Spectra, and pH Range (Sunthankar, Gilman)*	9	574
Birefringence (Fibers): *See* **Fibers; Synthetic Fibers**		
Blending: *See* **Cotton**		
Carbon Arc Light: *See* **Cotton and Other Textiles**		
Carboxymethylated Cotton: *See* **Cotton**		
Card: *See* **Fiber Fineness (Micronaire)**		
Cellulose, The Homogeneous Degradation of (Letter to the Editor) (Spurlin)	10	693
See **Cellulose Studies**		
Cellulose, The Oxidation of, by Ozone in Small Concentrations (Bogaty, Campbell, Appel)	2	81
"Cellulose, The Reaction of, with Formaldehyde," by Wagner and Pacsu (Letter to the Editor) (Nickerson)	8	554
Cellulose, Some Observations on the Evaporation of Water from (Bogaty, Campbell, Appel)	2	75
Cellulose Acetate, Studies on: Part III: Combination of Sulfuric Acid During the Acetylation of Cellulose and the Mechanism of Acetylation (Araki)*	10	630

* Parts I and II were published in *The Journal of Organic Chemistry.*

* Parts I and II were published in *Cellulosechemie.*

	No.	Page
Cellulose Ethers, Formation of, in Water-Repellency Treatment of Cotton with Stearamidomethylpyridinium Chloride (Schuyten, Weaver, Frick, Reid)	6	424
Cellulose Fibers, Enzymic Degradation of (Blum, Stahl)	3	178
Cellulose Studies*		
Part XVI: The Reaction of Cellulose with Formaldehyde (Wagner, Pacsu)	1	12
Part XVII: The Heterogeneous Acid Degradation of Cellulose (Bauer, Pacsu)	6	385
Part XVIII: The Homogeneous Degradation of Cellulose in Phosphoric Acid (Bauer, Pacsu)	6	397
See **Cellulose**		
Centrifuge Studies: *See* **Swelling Capacities**		
Chromatography: *See* **Silk Fiber**		
Colorimetry: *See* **Cotton Fiber**		
Conifer Tracheids: *See* **X-Rays**		
Consumer Quality Characteristics (Cotton): *See* **Cotton**		
Cordage Fibers and Yarns: *See* **Elastic Performance**		
Cords: *See* **Microscopic Examination; Tire Cords**		
Cotton, An Analysis of the Consumer Quality Characteristics of: Implications for Research (Buck) (T.R.I. Annual Meeting, 1951)	2	117
Cotton, Blending of, by Fineness Determination and Other Applications of Research in Mill Operation (Regnery) (T.R.I. Annual Meeting, 1951)	1	49
Cotton, Check Sample Testing of Physical Properties of, with Instruments (Hopper)	7	472
Cotton, Effects of Mechanical Processing of, on the Physical Properties of Fibers (Grant, Morlier, Scott)	10	682
Cotton, Greige, Some Observations on the Wetting of (Wolfrom, Nuessle)	4	246
Cotton, Partially Carboxymethylated, Crease-Resistant Cloth from (Daul, Reinhardt, Reid)	12	792
Cotton, Raw, Influence of Cross-Sectional Shape of, on Dimensional Changes in Mercerization Without Tension (Orr, Humphreys, Grant)	2	89
Cotton, Studies on the Partial Carboxymethylation of (Daul, Reinhardt, Reid)	12	787
Cotton: *See also* **Cellulose Ethers; Shrinkage in Laundering; Swelling of Cotton Fibers**		
Cotton Cellulose, Action of Cyanuric Chloride on (Warren, Reid, Hamalainen)	9	584
Cotton Defoliation and Fiber Maturity (Grimes)	10	637
Cotton Fabrics, Development of a Sewability Test for (Frederick)	10	687
Cotton Fabrics, Partially Acetylated, Heat-Resistance of (Honold, Poynot, Cucullu)	1	25
Correction	3	222
Cotton Fiber, Colorimetric Determination of the pH of (Pons, Hoffpauir)	3	200
Cotton Maturity: *See* **Cotton Defoliation**		
Cotton and Other Textiles, Effects of Unfiltered Carbon Arc Light in Accelerated Weathering of (Dean, Fleming, O'Connor)	9	609
Cottons and Modified Cottons, Nonfreezing Water and Nonfreezing Benzene Capacities of (Magne, Skau)	11	748
Crease-Resistance: *See* **Cotton**		
Cuticula: *See* **Wool**		
Cyanuric Chloride: *See* **Cotton Cellulose**		
Cysteine: *See* **Stress Relaxation**		
Degradation: *See* **Cellulose; Cellulose Fibers; Cellulose Studies**		
Density, Yarn and Fabric, Some Theoretical Aspects of (Hoffman)	3	170
Density Gradient Columns, The Use of, for the Determination of Specific Gravity (Letter to the Editor) (Lindsley)	4	287
Desiccation Rate: *See* **Swelling Capacities**		
Diffusion, Adsorption-Controlled, in a Solid, A Numerical Solution of the Differential Equation for (Fujita)	4	281
Correction (Letter to the Editor)	8	556
Diffusion, Concentration-Dependent, The Exact Pattern of a, in a Semi-infinite Medium (Fujita)		
Part I	11	757
Part II	12	823
Diffusion Coefficient, A Method of Determining the Concentration Dependence of the (Letter to the Editor) (Fujita, Kishimoto)	2	94
Dimensional Changes: *See* **Cotton; Keratin; Shrinkage in Laundering; Swelling**		
Dyeing: *See* **Azo Dyes; Wet Processing**		
Dyes: *See* **Azo Dyes**		
Elastic Performance of Textile Materials, Mechanics of†		
Part VIII: Graphical Analysis of Fabric Geometry (Painter)	3	153
Correction	8	557
See **Fabric Geometry Graph**		
Part IX: Factors Affecting the Translation of Certain Mechanical Properties of Cordage Fibers into Cordage Yarns (Platt, Klein, Hamburger)	10	641
Supplement to Part IX (Letter to the Editor)	12	827
Part X: Some Aspects of Elastic Behavior at Low Strains (Hamburger, Platt, Morgan)	11	695
Correction	12	827
Electrical Resistance Measurements on Fibers and Fiber Assemblies (Hersh, Montgomery)	12	805
Electron Microscope Objective, The High-Contrast (Wide-Field), and Fiber Replicas (Morehead)	6	379
Emulsions: *See* **Silk Soaking Emulsions**		
Ethers: *See* **Cellulose Ethers**		
Fabric Geometry: *See* **Elastic Performance; Shrinkage in Laundering**		
Fabric Geometry Graph, Locating a Fabric on the (Letter to the Editor) (Painter)	8	556
See **Elastic Performance**		
Fabrics, Thermoplastic Fiber-Bonded, Some Properties of (Wrotnowski)	7	486
Fabrics, Water-Resistant, A Theory of (Segall)	11	730
Fabrics: *See also* **Cotton; Cotton Fabrics; Density; Elastic Performance; Microscopic Examination; Nylon Oxford Cloth "41"; Rayon Fabrics; Screens and Fabrics; Shrinkage; Wet Processing**		
Fat Content: *See* **Silk Soaking Emulsions**		
Ferroxyl Reagent: *See* **Knitting Needle Corrosion**		
Fiber Cross-Sectional Area, The Vibroscopic Method for Determination of (Montgomery, Milloway)	11	729
Fiber Fineness (Micronaire), Neps in Card Web, and Yarn Appearance Grades (Marth, Arthur, Berkley)	9	561
Fibers, Double Refraction Measurement of (Letter to the Editor) (de Vries)	9	619
Fibers: *See also* **Cellulose Fibers; Cotton; Cotton Defoliation; Cotton Fiber; Elastic Performance; Electrical Resistance Measurements; Electron Microscope Objective; Fabrics; Jute Fiber; Silk Fiber; Sorption; Staple Fiber Mixtures; Stress Relaxation; Swelling; Swelling Capacities; Swelling of Cotton Fibers; Synthetic Fibers; Wools**		
Fibrograph, Use of a Servo System for Automatic Operation of the (Tallant)	9	617
Fineness: *See* **Cotton; Fiber Fineness (Micronaire)**		
Finishing, Textile, The Principles of (Valko)	3	213
Formaldehyde: *See* **Cellulose; Cellulose Studies**		
Fractionation: *See* **Silk Fiber**		
Greige Cotton: *See* **Cotton**		
Hair, Stretched, The α-β Transformation in (Elliott)	12	783
Hair: *See also* **Swelling of Human Hair**		
Heat-Resistance: *See* **Cotton Fabrics**		
Hemicellulose: *See* **Jute Fiber**		
Humidity: *See* **Swelling**		
Hydrolysis: *See* **Silk Fiber**		
Jute Fiber, The Nature of the Hemicelluloses of: Part I (Sarkar, Mazumdar, Pal)	8	529
Keratin, The Supercontraction of (Mercer)	7	476
Knitting Needle Corrosion, The Ferroxyl Reagent Applied to a Study of (Letter to the Editor) (Bryant)	8	553
Laundering: *See* **Shrinkage in Laundering**		
Letters to the Editor: *See* **Cellulose; Density Gradient Columns; Diffusion; Diffusion Coefficient; Elastic Performance; Fabric Geometry Graph; Fibers; Knitting Needle Corrosion; Silk Soaking Emulsions; Tire Cords; Twill Weaves; Wool; X-Rays**		
Measurements: *See* **Cotton; Cotton Fiber; Density Gradient Columns; Electrical Resistance Measurements; Fiber Cross-Sectional Area; Fibers; Silk Soaking Emulsions; Swelling Capacities**		
Mechanical Damage: *See* **Abrasion of Textiles; Wet Processing; Wools**		
Mechanical Home Washers: *See* **Washers**		
Mechanical Processing: *See* **Cotton; Servomechanism Techniques; Wet Processing; Wools**		
Mechanical Properties: *See* **Elastic Performance; Polyamide Monofils; Rayon Fabrics; Stress Relaxation; Swelling of Cotton Fibers; Synthetic Fibers; Tire Cords; Warping; Washers; Yarn Load-Elongation Recorder; Yarns**		
Mercerization: *See* **Cotton**		
Mercerization of Yarn—Experimental Apparatus and Techniques (Goldthwait, Murphy, Lohmann, Smith)	8	540
Micronaire: *See* **Fiber Fineness (Micronaire)**		
Microscopic Examination, A Method of Repetitive Longitudinal Sectioning of Cords and Fabrics for (Davis)	3	192
Microscopy: *See* **Electron Microscope Objective; Wool**		
Mill Operation: *See* **Cotton**		
Monofilaments: *See* **Polyamide Monofils**		
Neps: *See* **Fiber Fineness (Micronaire)**		
Nonfreezing Benzene Capacity (Cotton): *See* **Cottons and Modified Cottons**		
Nonfreezing Water Capacity (Cotton): *See* **Cottons and Modified Cottons**		
Nylon: *See* **Shrinkage in Laundering**		
Nylon Oxford Cloth "41," The Behavior of, on Pyrolysis (Hasselstrom, Coles, Balmer, Hannigan, Keeler, Brown)	11	742
Nylon Yarns, Spun, Sizing of, with Various Agents (Langston)	2	111
Oxidation: *See* **Cellulose**		
Ozone: *See* **Cellulose**		

* Part I appeared in the Oct., 1945, issue; Parts II–VIII in the Mar., Apr., June, July, Aug., Oct., and Nov., 1946, issues; Part IX in the Aug., 1947, issue; Part X in the July, 1948, issue; Parts XI and XII in the Oct. and Nov., 1949, issues; and Parts XIII–XV in the Dec., 1949, issue.

† Parts I and II appeared in the Feb. and Dec., 1948, issues; Part III in the Jan., 1950 issue; Parts IV and V in the Aug., 1950, issue; Part VI in the Oct., 1950, issue; and Part VII in the May, 1951, issue.

	No.	Page
pH: *See* **Azo Dyes; Cotton Fiber**		
Phosphoric Acid: *See* **Cellulose Studies**		
Physical Properties: *See* **Cotton; Density; Density Gradient Columns; Fabrics; Wools; Synthetic Fibers; Twill Weaves**		
Polyamide Monofils, Forced Vibrations of (Eyring, Alder, Rossmassler, Christensen)	4	223
Proteins, The Molecular Size of, from Several Wools Solubilized in Aquequeous Urea (Ward)	6	405
Pyrolysis: *See* **Nylon Oxford Cloth "41"**		
Rayon, Staple: *See* **Shrinkage in Laundering**		
Rayon Fabrics, Factors Affecting the Properties of (Jameson, Whittier, Schiefer)	9	599
Refractive Index (Fibers): *See* **Fibers; Synthetic Fibers**		
Research: *See* **Cotton; Textile Industry**		
Research and Development, Textile, Review of, During 1951 (Textile Research Institute Staff)	5	293
Research Interest, Applied, Building Our National Scientific Capital to Yield, for Industry in the Future (Waterman) (T.R.I. Annual Meeting, 1951)	1	69
Research Pays Off (Newton) (T.R.I. Annual Meeting, 1951)	1	65
Roving: *See* **Sliver and Roving**		
Screens and Fabrics, Aerodynamic Properties of (Hoerner)	4	274
Sectioning (Cords and Fabrics): *See* **Microscopic Examination**		
Sericin: *See* **Silk Fiber**		
Servo System: *See* **Fibrograph**		
Servomechanism Techniques, Practical Application of, to a Process-Control Problem (Higgins, McKnight)	3	203
Sewability Test: *See* **Cotton Fabrics**		
Shrinkage: *See* **Stress Relaxation**		
Shrinkage in Laundering, The Geometry of Knit Fabrics Made of Staple Rayon and Nylon and Its Relationship to (Fletcher, Roberts)	7	466
Shrinkage in Laundering, The Geometry of Plain and Rib Knit Cotton Fabrics and Its Relation to (Fletcher, Roberts)	2	84
Silicon Dyes: *See* **Azo Dyes**		
Silk Fiber, Chromatographic Studies of the (Bryant)		
Part I: The Amino Acid Composition of Two Sericin Fractions	8	523
Part II: Fractionation of a Fibroin Hydrolyzate	8	525
Silk Soaking Emulsions, Determination of the Fat Content of (Letter to the Editor) (Bryant)	6	433
Sizes, Textile, The Evaluation of (King, Weil, Condo, Rutherford)	9	567
Sizes: *See also* **Nylon Yarns**		
Sliver and Roving, An Evaluation of Long- and Short-Term Variation in (Simpson, Landstreet, Corley)	1	42
Sodium Chlorite: *See* **Wool**		
Sonic Home Washers: *See* **Washers**		
Sorption of Synthetic Surface-Active Compounds by Textile Fibers (Weatherburn, Bayley)	12	797
Staple Fiber Mixtures, Analysis of (Fisher, Roberts)	8	509
Stearamidomethylpyridinium Chloride: *See* **Cellulose Ethers**		
Stress Relaxation of Fibrous Materials		
Part I: Instrumentation and Preliminary Results (Kubu)	12	765
Part II: Kinetics of the Reduction of Wool Keratin by Cysteine (Kubu and Montgomery)	12	778
Stress Relaxation and Shrinkage in Fibers (Chen, Ree, Eyring)	6	416
Sulfuric Acid: *See* **Cellulose Acetate**		
Surface-Active Compounds: *See* **Sorption**		
Swelling, Cross-Sectional, of Some Common Fibers, A Method for Studying the Effect of Humidity on the (Morehead)	8	535
Swelling Capacities of Fibers in Water		
Part I: Desiccation Rate Measurements (Welo, Ziifle, Loeb)	4	254
Part II: Centrifuge Studies (Welo, Ziifle, McDonald)	4	261
Swelling of Cotton Fibers, Effects of Tension on the (Giuffria, Tripp)	1	21
Swelling of Human Hair in Water and Water Vapor (Stam, Kratz, White)	7	448
Synthetic Fibers, Observations of the Birefringence and Refractive Index of, with Special Reference to Their Identification (Heyn)	8	513
Synthetic Fibers, Properties of Fabrics Made from Several, and Their Impact on the Textile Industry (Lake) (T.R.I. Annual Meeting, 1951)	2	138
Synthetic Fibers, The Role of, in the Textile Industry of the Future (Ray) (T.R.I. Annual Meeting, 1951)	2	144
Tensiometer: *See* **Yarn Tensiometer**		
Testing: *See* **Abrasion of Textiles; Cotton; Cotton Fabrics**		
Textile Industry, Position of the, in Relation to Research and Development (Wells) (T.R.I. Annual Meeting, 1951)	1	53
Textile Industry, Technical Problems of (Fox) (T.R.I. Annual Meeting, 1951	1	60
Thermoplastic Fabrics: *See* **Fabrics**		
Tire Cords, Fatigue of, as a Function of Twist (Letter to the Editor regarding an article by Budd) (Hermanne, Quintelier)	2	95
Author's Comments (Budd)	2	97
Twill Weaves, Cover Factor Adjustments for (Letter to the Editor) (Backer)	6	435
Twist, Optimal, in Staple Yarn (Alexander)	8	503
Twist: *See also* **Tire Cords**		
Urea: *See* **Proteins**		
Vibroscope, An Improved (Dart, Peterson)	12	819
Vibroscope: *See also* **Fiber Cross-Sectional Area**		
Warping, Some of the Factors Influencing Yarn Tension in (Dyer, Faw, Beard)	7	487
Washers, Home, Sonic and Mechanical, A Comparative Study of: Part I: Strength and Dimensional Changes (Mack, Balog, Jordan)	1	30
Water-Resistance: *See* **Cellulose Ethers; Fabrics**		
Weathering: *See* **Cotton and Other Textiles**		
Weaves: *See* **Twill Weaves**		
Wet Processing, Relation Between Certain Defects in Dyed Fabrics and Mechanical Damage in (Cates, Campbell, Rutherford)	10	623
Wetting: *See* **Cotton**		
Wool, The Treatment of, with Sodium Chlorite (Earland, Johnson)	9	591
Wool, The Visibility of the "Cuticula" of, Under the Phase-Contrast Microscope (Letter to the Editor) (Algera)	2	97
Wools, Apparel, Properties of		
I. Preliminary Report on Worsted Processing Trials (von Bergen, Wakelin) (T.R.I. Annual Meeting, 1951)	2	123
II. Modification of Fiber Surface During Worsted Processing (O'Reilly, Whitwell, Steele, Wakelin)	7	441
Wool: *See also* **Hair; Proteins**		
Wool Keratin: *See* **Keratin; Stress Relaxation**		
Worsted: *See* **Wools**		
X-Rays, The Low-Angle Scattering of, by Conifer Tracheids (Letter to the Editor) (Wardrop)	4	288
Yarn Appearance Grades: *See* **Fiber Fineness (Micronaire)**		
Yarn Load-Elongation Recorder, An Automatic (Breazeale, Irvin)	8	549
Yarn Tensiometer, A High-Speed Recording (Nistico, Sprague, Work)	2	99
Yarns, Bent, The Mechanics of (Backer)	10	668
Yarns: *See also* **Density; Elastic Performance; Mercerization; Nylon Yarns; Twist; Warping**		

Book Reviews

	No.	Page
Adhesion and Adhesives. N. A. de Bruyne and R. Houwink, editors (1951)	8	560
Carbon Compounds, Chemistry of: Vol I, Part A: General Introduction. E. H. Rodd, editor (1951)	11	761
Chemical Analysis, Physical Methods in: Vol. II. Walter G. Berl, editor (1951)	6	439
Chemistry Carbohydrate, Advances in: Vol. VI. C. S. Hudson and S. M. Cantor, editors (1951)	9	621
Chemistry, Organic, Holleman's. Revised by J. P. Wibaut (1951)	8	559
Cotton from Field to Fabric. 5th Ed. National Cotton Council (1951)	2	152
Crystal Structures. First Supplement to Vols. I and II. Ralph G. Wyckoff (1951)	8	559
Dangerous Materials, Handbook of. N. Irving Sax, assisted by M. J. O'Herin and W. W. Schultz (1951)	7	501
Dyeing and Printing, The Chemical Technology of: Vol. II. Louis Diserens. Translated and revised from the 2nd German Ed. by Paul Wengraf and Herman P. Baumann (1951)	8	559
Fabrics, Know Your. Lucy D. Taylor (1951)	2	152
Fibres, Man-Made, The Development of Some. A. R. Urquhart, H. J. Hegan, and G. Loasby (1952)	11	761
Finishing, Textile, An Introduction to. J. T. Marsh (1951)	9	621
Flameproofed Textiles, Standard for. NFPA No. 701. NFPA Committee on Flameproofing and Preservative Treatments (1951)	6	439
Microscopy, Phase—Principles and Applications. Alva H. Bennett, Helen Jupnik, Harold Osterberg, and Oscar W. Richards (1951)	7	499
Plastics and Glass, The Strength of. R. N. Haward (1949)	6	437
Polymers, High, Natural and Synthetic. 2nd Ed. K. H. Meyer (1950)	6	437
Polymers, Vinyl and Related. Calvin E. Schildknecht (1952)	11	762
Radioisotopes; Industrial Applications. G. H. Guest (1951)	7	499
Statistics, Technological Applications of. L. H. C. Tippett (1950)	6	438
Synthetic Textiles, American Handbook of. Herbert R. Mauersberger, editor (1952)	11	763
Textile Inter-Fiber Competition 1937 & 1949. Supplement to *Rayon Organon* (1951)	2	151
Textile Materials, Identification of. 3rd Ed. The Textile Institute (1951)	6	438
Textile Printing. Fred F. Jacobs (1952)	11	764
Textile Progress, Review of: Vol. I: 1949. The Textile Institute (1950)	2	151
Textile Progress, Review of: Vol. II. The Textile Institute and the Society of Dyers and Colourists (1951)	11	762
Wood, Chemistry of. Erik Hägglund (1951)	9	622
Wool Dyeing, The Theory and Practice of. C. L. Bird (1951)	7	500

RNAL

Page
261
21
448
513
138
144
53
60
95
97
435
503
819
487
30
623
591
97
123
441
288
549
99
668
Page
499
437
437
762
499
438
763
151
438
764
151
762
522
500